CELLULOSE CHEMISTRY AND TECHNOLOGY

ISOLATION AND CHARACTERIZATION OF MICROCRYSTALLINE CELLULOSE FROM FENNEL STEMS AGRO-WASTE

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For the current work, cellulose was isolated from the stems of fennel (*Foeniculum vulgare* Mill.), using combined chemical treatments such as dewaxing, delignification, and bleaching. The extracted cellulose was successfully used for the preparation of microcrystalline cellulose (MCC) by the acid hydrolysis process. For the comparative study, the obtained fennel stem (FS) microcrystalline cellulose (FS-MCC) was characterized along with the raw fennel stem (RFS) and fennel stem cellulose (FS-C). The chemical composition study confirmed that the content of α-cellulose in RFS increased from 45.75% to 59.64% in FS-MCC. Further, FS-MCC was examined by Fourier transform infrared (FT-IR) spectroscopy, which confirmed an improved structure of α-cellulose. X-ray diffraction (XRD) analysis confirmed that crystallinity increased from 37% to 74%. The scanning electron microscopy (SEM) showed a rough surface and a reduction in the fibre size that indicates the complete removal of non-cellulosic constituents from FS-MCC. Differential scanning calorimetry (DSC) proved that the isolated FS-MCC had a high thermal degradation temperature (393.77 °C), compared to the RFS (336.54 °C). In addition to this, Brunauer-Emmett-Teller (BET) analysis of FS-MCC showed higher surface area and total pore volume (1.49 m^2g^{-1}, 0.0028 cm^3g^{-1}) compared to the of FS-C (0.39 m^2g^{-1}, 0.0024 cm^3g^{-1}). In the view of overall results, the prepared FS-MCC could offer great potential in future applications.

Keywords: acid hydrolysis, fennel stems, microcrystalline cellulose, properties

INTRODUCTION

Fennel (*Foeniculum vulgare* Mill.) is a well-known kitchen herb that is extensively used across central Asia, Mediterranean region to Northern Africa. Being an essential spice in Indian cuisine, fennel holds cultural significance across numerous Indian households. The fennel plant belongs to the Apiaceae family having erect, glaucous green hollow stems that grow to a height of up to 2.5 meters.[1] Fennel seeds are predominantly utilized as a spice as well as in the preparation of medicinal products due to its dietary fibre content and several healthy flavonoid compounds. It is a perennial herb mostly cultivated in the tropics and subtropics area, where it plays a significant role in both agricultural and economic systems. In terms of total world fennel production, India contributes 60% of the world's estimates, which is approximately 584,000 tons per year.[2] Though it is a versatile spice, the stalks and stems of fennel plant end up as agricultural waste and remain largely untapped, despite being a storehouse of bioactive substances like polyphenols, and of cellulose, hemicelluloses and lignin. Thus, the discarded fennel stalks and stems can be potentially harvested for the sustainable output of these compounds reiterating the waste to energy approach. The members of Apiaceae family have been reported to be composed of 53.3% cellulose.[3] Still, fennel stems remain largely unexplored, therefore in the present study, they were utilized as a raw material for extracting cellulose.

Cellulose is the most abundant natural polymer that constitutes the primary cell wall of lower and higher plants. Cellulose contains a polydispersed linear chain of β-(1→4)-glycosidic bond linked D-glucopyranose monomer units. The presence of intra- and intermolecular hydrogen bonds renders it more stable and highly crystalline.[4-6] Cellulose and cellulose-based polymers are widely used as animal feed, construction material, and in

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numerous industries, such as pulp and paper, textiles, pharmaceuticals and cosmetics, as an easily available and inexpensive raw material.[7,8] Cellulose usage is steadily rising due to recent environmental legislation as well as consumer pressure on manufacturing industries (particularly automotive, construction and packaging) to search for ecologically friendly materials.

Crystalline cellulose has been reported to exhibit high mechanical strength with an elastic modulus in axial direction of ≈110–220 GPa, which is almost comparable to that of carbon fibres, Kevlar-49 fibres and clay nanoplatelets.[9] Several types of cellulose particles, like cellulose nanocrystals,[10] cellulose nanowhiskers,[11] microcrystalline cellulose[12] and microfibrillated cellulose,[13] have been obtained from various cellulose source materials. The polymer features like crystallinity, aspect ratio, crystal structure, and morphology of the cellulose particles extracted depend on the cellulose sources and extraction methods employed.[14,15]

Microcrystalline cellulose (MCC) is an inodorous, tasteless crystalline micrometric powder widely known for its biocompatibility, biodegradability, and mechanical strength.[16] Conventionally, MCC is extracted by mineral acid treatment of α-cellulose, which leads to the dissolution of non-cellulosic constituents.[17-19] Due to its superior characteristics, including mechanical strength, low density, large surface area, renewability and non-toxicity, MCC has attracted attention from both research and industrial sectors, such as pharmaceuticals, cosmetics and personal care, and plastic industries, which has skyrocketed its demand.[20-24] Another impressive application of MCC is as a green adsorbent – its strong hydrogen bonding renders it an ideal framework for adsorbents synthesis.[34] Having three functional hydroxyl groups in its repeating unit, it is an ideal candidate for desired modification by typical alcohol groups, whose oxidation enables easy binding of carboxyls from target compounds.[35] Owing to its different particle size and micro-fibrils networks, MCC have versatile applications in bio-composites, protein immobilization, drug delivery, and metallic reaction templates.[36]

The global microcrystalline cellulose (MCC) market size was estimated at 885.1 million USD in 2018, expected to reach 1241.4 million USD by 2023.[25] The limited availability of wood pulp, the conventional source, has compelled industries to search for alternatives for the production of cellulose and its derivatives. Hence, recent research has focused on a variety of untapped lignocellulosic raw materials as cheaper and more sustainable resources for extracting MCC by harnessing agro-waste streams into high value-added products. Numerous studies reported employing orange mesocarp,[26] jute,[27] fodder grass,[28] alfa grass fibres,[29] soybean hulls,[30] rice husk,[31] cotton wool,[32] roselle fibres,[33] *etc*. for MCC extraction.

The objective of the present study has been to investigate the potential of fennel stems as a source for isolating microcrystalline cellulose (MCC). To the best of the authors' knowledge, hitherto, fennel stems have not been investigated for cellulose extraction and preparation of MCC, but could be harnessed as an effective waste-to-energy approach. FMCC was characterized by various spectral and analytical methods. The Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), Brunauer–Emmett–Teller surface area analysis (BET) and differential scanning calorimetry (DSC) were conducted to characterize the structure of the MCC at various stages of this study.

EXPERIMENTAL

Materials

Fennel stems were collected from a local farm in Amreli district, Gujarat, India. To remove impurities (dust, dried seeds, leaves *etc*.), the stems extensively washed with tap water, followed by drying at 50 °C for 24 h. The dried fennel stem was ground and sieved to an average particle size of 5 mm and stored in a container at ambient temperature for further use. Chemicals, such as n-hexane, sodium hydroxide, maleic acid, citric acid, sodium chlorite, methanol, hydrogen peroxide, sodium bisulfite, acetic acid, H_2SO_4, and HCl were of analytical grade and used without further purification for the present work.

Cellulose extraction from fennel stem

The extraction of cellulose was carried out using a previously reported method by Hapani *et al.*[1] The cellulose extraction process involved mainly three steps: i) dewaxing: performed with an n-hexane:ethanol (2:1 V/V) in Soxhlet apparatus at 60 °C for 10 h (the dewaxed samples were sieved and washed with distilled water (DW)): ii) delignification: performed on a magnetic stirrer using different concentration of sodium hydroxide (sample to liquor ratio 1:10): 2%, 4%, 6%, 8%, and 10%, with different soaking time 1 h, 2 h, 3 h, 4 h, and 5 h at different temperature of 55 °C, 65 °C, 75 °C, 85 °C, and 95 °C, respectively, for the optimization of the cellulose extraction process for the current work;

iii) bleaching treatment: performed using 2% H_2O_2 with different concentrations of citric acid (5%, 10%, 15%, 20%, and 25%); the mixture was shaken for 4 h at 60 °C.

Based on the results obtained, the optimized method for delignification was considered the treatment with 4 wt% NaOH solution at 55 °C for 4 h, followed by bleaching with 2% H_2O_2 and 20% citric acid. The obtained cellulose was dried at 50 °C for 12 h and was kept in airtight containers, labelled as fennel stem cellulose (FSC).

Preparation of microcrystalline cellulose (MCC) using fennel stem cellulose (FSC)

The cellulose recovered from fennel stems was used for obtaining microcrystalline cellulose by using the acid hydrolysis process reported by Tarchoun *et al*.[37] 1 g of FSC was introduced into a 50 mL beaker, mixed with an aqueous solution of 2.5M HCl, 2.5M HNO_3, 2.5M H_2SO_4 (20 mL) respectively, and stirred continuously at 100 °C for 30 min. The samples were strained and excessively washed with DW until neutralization, followed by oven drying at 50 °C for 24 h to obtain fennel microcrystalline cellulose (FMCC). Figure 1 shows schematic presentation of microcrystalline cellulose preparation from fennel cellulose. FMCC yield was determined by using Equation (1):[37]

$$\text{MCC Yield (\%)} = \frac{W_f}{W_i} \times 100 \qquad (1)$$

where W_f is the weight of recoverd FMCC, W_i is the initial weight of FSC.

Characterization

Chemical composition analysis

The chemical composition of the samples was ascertained as reported in previous literature.[38-40]

Holocellulose content (cellulose + hemicelluloses): the holocellulose content is primarily determined by the removal of lignin from the samples. The dewaxed samples (3 g) were treated with 0.7% $NaClO_2$ (sodium chlorite) solution at 80 °C for 2 hours under continuous stirring on a magnetic stirrer and pH 4.0 was maintained using acetate buffer. The resultant slurry was strained and then rinsed with 2% $NaHSO_3$ (sodium bisulfite). After washing with DW three times, the pulp was oven-dried at 105 °C for four hours. At this point, the resultant dry powder contained hemicelluloses and cellulose. The content of the latter was determined by treating it (3 g) initially with 35 mL of 17.5% NaOH sodium hydroxide solution (5.24 M), and then after about 10 minutes, a further 40 mL of the same solution was added slowly with constant stirring at ~80. The above mixture was rinsed generously with nearly 1 L of DW and then immersed in a 10% acetic acid solution for 10 minutes. This sample was further washed with DW until neutralization and then placed in the oven for 4 hours at 60 °C. The dried sample contained only cellulose. From the difference between holocellulose and cellulose content, the amount of hemicelluloses was calculated.

Lignin content: the lignin of the dewaxed sample was estimated by treating it with 72% H_2SO_4 for 48 hours at 20 °C. The slurry was strained and rinsed thrice with DW. The obtained product was oven-dried at 105 °C until it was completely dried.

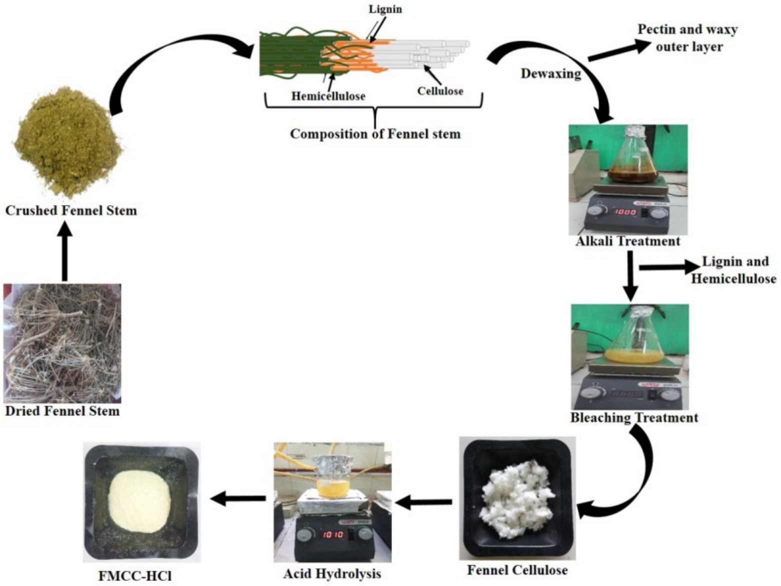

Figure 1: Experimental set-up for preparation of fennel microcrystalline cellulose (FMCC-HCl)

Structural analysis (FTIR)

The differences in the composition of raw fennel stems (RFS), FSC, and FMCC were evaluated using Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of RFS, extracted FSC, and FMCC were recorded on a Bruker Alpha-II ATR-FTIR Spectrophotometer (Germany). The absorption was measured over the range of 4,000-600 cm^{-1} with a resolution of 4 cm^{-1} for each sample using 32 scans.

Crystallinity (XRD)

The diffraction patterns and crystallinity index of all the cellulose and MCC samples were determined with a Rigaku Ultima IV Powder X-ray Diffractometer (XRD) (Tokyo, Japan) using CuKα1 radiation at the wavelength λ = 1.54 A°, current of 45 mA, accelerating voltage of 40 kV and a scanning rate of 6°/min, with a step size of 0.02°. The diffraction intensities were measured between Bragg angles (2θ) of 5–60°. The crystallinity index (Crl) of the samples was determined using Equation (2):[41]

$$\mathrm{Crl}\,(\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100 \qquad (2)$$

where Crl – the crystallinity index, I_{200} – total peak intensity area of the 200 lattice plane having contribution of both crystalline and amorphous regions, I_{am} – the peak intensity contribution from the amorphous region.

Thermostability (DSC)

The thermal stability of all the samples was determined using a Shimadzu DSC-60 Plus (Kyoto, Japan) differential scanning calorimeter (DSC). Around 7 mg samples were heated from 30 °C to 400 °C at a constant rate of 10 °C/min using nitrogen (N) gas.

Surface morphology (SEM)

The surface morphology characteristics of the cellulosic samples were captured as micrographs using an XL 30 ESEM EDAX Scanning Electron Microscope (Philips, Netherland) under an escalating voltage of 10 kV (samples mounted using carbon tape).

Surface area and pore volume

The surface characteristics of FSC and FMCC-HCl were studied by BET analysis (by nitrogen (N_2) gas adsorption at 77 K) in a BELSORP MAX G (Mocrotrac MRB, Japan) gas adsorption analyzer. The degassing of all the samples was performed at 90 °C for 12 h. The isothermal data obtained from the gas adsorption analyzer using the Brunauer-Emmett-Teller (BET) Surface Area Analyzer and the Barrett-Joyner-Halenda (BJH) method were used to determine the mesopore volume, external surface area, and mesopore surface area of these samples.

RESULTS AND DISCUSSION

Chemical composition

The chemical composition analysis was used to determine the % amount of α-cellulose, hemicelluloses, and lignin of all the samples. Table 1 summarizes the average values of chemical composition of all the samples. To ensure accuracy, triplicate measurements were performed. The treatments applied to the samples disengaged the linkages among cellulose, hemicelluloses, and lignin, leaving behind pure crystalline cellulose. The remaining hemicelluloses and lignin were further separated through the bleaching treatment. The acid neutralization of the fennel stem cellulose (FSC) benefits in the individualization of microfibrils from the cell wall.[42] The results showed that the α-cellulose content increased in fennel microcrystalline cellulose (FMCC) in comparison to raw fennel stem (RFS) and FSC. Therefore, fennel stems can be used as a potential source for microcrystalline cellulose preparation.

Yield percentage of microcrystalline cellulose (MCC)

The acid hydrolysis process is usually preferred for the preparation of microcrystalline cellulose, as it is less time-consuming than other procedures. The FMCC preparation was carried out using three different acids: HCl, HNO_3, and H_2SO_4, using the same concentration (2.5 M) and the same reaction time (30 min). The highest yield (82.60%) was recovered using 2.5M HCl, while 2.5M HNO_3 and 2.5M H_2SO_4 gave 75.20% and 70.10%, respectively. Therefore, for the preparation of MCC from fennel cellulose, 2.5M HCl was found to be more suitable than the other acids.

The recovered yield of F-MCC was calculated and compared with those reported in the literature for other agro-wastes and the data have been tabulated in Table 2.

Table 1
Chemical composition of RFS, FSC, and FMCC

Samples	α-Cellulose (%)	Hemicellulose (%)	Lignin (%)
RFS	45.75 (±0.23)	31.08 (±0.15)	22.01 (±0.18)
FSC	54.05 (±0.11)	8.63 (±0.17)	10.40 (±0.22)
FMCC	59.64 (±0.16)	6.67 (±0.17)	6.80 (±0.07)

The values represent the means ± S.E. (n=3)

Table 2
Comparison of fennel stem MCC yield obtained from different agro-waste sources

Source	Conditions of hydrolysis	Yield recovery of MCC	Refs
Fennel stem	2.5M HCl at 100 °C for 30 min	82.60%	Present work
Kapok pods	2.5N HCl at 100 °C for 30 min	22.58%	55
Belulang grass	2.5N HCl at 70 °C for 90 min	74.89	56
Conocarpus fibre	2.5N HCl at 80 °C for 30 min	27%	57
Teff straw	2.5N HCl at 105 °C for 30 min	77.4%	58
Sengon wood sawdust	4N HCl at 80 °C for 4 h	85.01%	59
Washingtonia fibre	2.5N HCl at 80 °C for 30 min	25%	60

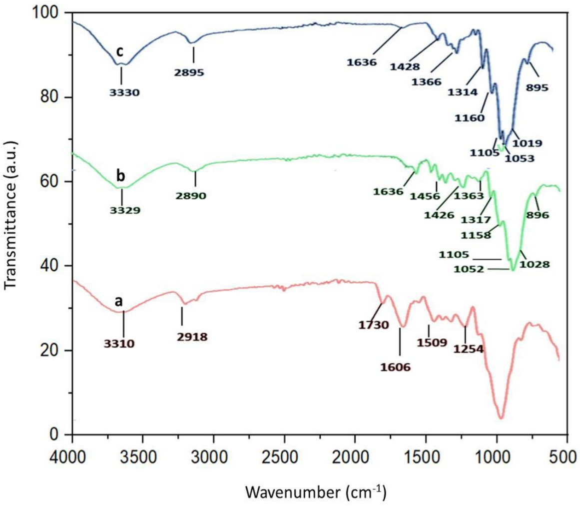

Figure 2: FTIR spectra of (a) RFS, (b) FS-C, (c) FMCC-HCl

Structural analysis

The structural analysis of RFS, FSC, and FMCC-HCl was performed by FT-IR to confirm the formation of MCC from fennel stem, as it can identify the functional groups and chemical changes that occurred after the chemical treatments applied. Figure 2 depicts the FT-IR spectra of RFS, FSC, and FMCC-HCl recorded in the range from 4000 to 400 cm^{-1}. The broad absorbance band appearing in all three spectra from 3300 cm^{-1} to 3500 cm^{-1} corresponds to the stretching vibrations of the -OH group, which is assigned to cellulose. This peak intensity increased from RFS to FMCC due to cleavage in the cellulose chain upon acid hydrolysis.[43] The absorption from 2900 cm^{-1} to 2800 cm^{-1} is assigned to the -C-H stretching vibrations, which relates to the crystalline structure of cellulose.[33] Moreover, the absorption band at 1730 cm^{-1} is related to acetyl or uronic ester groups of hemicelluloses and is present only in RFS – the absence of this peak in FSC and FMCC indicates the removal of hemicelluloses.[43] The absorption from 1600 cm^{-1} to 1640 cm^{-1} in all samples is due to the -OH bending of adsorbed water.[32]

The peak at 1509 cm^{-1} in the RFS can be assigned to the aromatic symmetrical stretching of the C=C group, which indicates the presence of lignin. The disappearance of this peak in FSC and FMCC is attributed to alkali treatment. Alkaline treatment interrupts the linkage between lignin and other carbohydrate fractions in the fennel sample.[44] The absorption bands at 1428 cm^{-1} and 1412 cm^{-1} correspond to -CH$_2$ scissoring and CH$_2$ bending vibration, respectively, which ascertain the crystallinity of cellulose. The FSMCC-HCl shows sharper peak intensity than that of the FSC sample, it indicates its higher crystallinity.[45] The absorbance from 1366 cm^{-1} to 1314 cm^{-1} in FSC and FMCC corresponds to the C-H asymmetric deformations. The peaks observed at 1160 cm^{-1} and 1158 cm^{-1} are related to the asymmetrical stretching of the C-O-C group. The band appeared at 1053 cm^{-1} and 1052 cm^{-1} is due to the vibrations of C-C, C-OH, and C-H ring. The intensity peak at 895 cm^{-1} corresponds to the C-H vibration of beta-glycosidic linkages in cellulose.[46] The hemicellulose and lignin components decreased after the given treatment, which leads to an increase in the α-cellulose content from RFS to FMCC-HCl, as proven by FT-IR analysis.

Crystallinity

The cellulose structure has both crystalline and amorphous regions, whereas hemicelluloses and lignin are only amorphous. X-ray diffraction (XRD) analysis was used to identify the phases in the samples as it can examine the structure of a single crystal or powder to determine the degree of crystallinity. The X-ray diffractograms of RFS, FSC, and FMCC-HCl are shown in Figure 3 and the crystallinity indices are tabulated in Table 3. All three diffractograms showed peaks at 2θ = 16.33°, 22.75°, and 34.97°, corresponding to crystallographic planes (110), (200), and (040) respectively.

From Table 2, it can be observed that the crystallinity index increases from RFS to FMCC. It is clear from Figure 3c that the peaks located at 22.75° in the diffractograms of FSC and FMCC-HCl become sharper and narrower, indicating an increase in cellulose crystallinity, owing to the removal of lignin and hemicelluloses due to cleavage of glycosidic linkages releasing crystallites.[47]

The crystallinity obtained is superior to the values reported for MCC in the literature for different biomass resources, like soybean hulls (70%),[48] corncob (52.82%),[17] date seeds (70%),[49] sago seed shells (67%)[6] and others. The higher crystallinity of FMCC-HCl indicates the efficient removal of non-cellulosic constituents by delignification, bleaching, and acid hydrolysis. After these treatments, cellulose intermolecular hydrogen bonds are rearranged and generate a compact structure that leads to higher crystallinity and rigidity of FSC and FMCC-HCl.[50] This increase in rigidity has been further supported by thermal analysis.

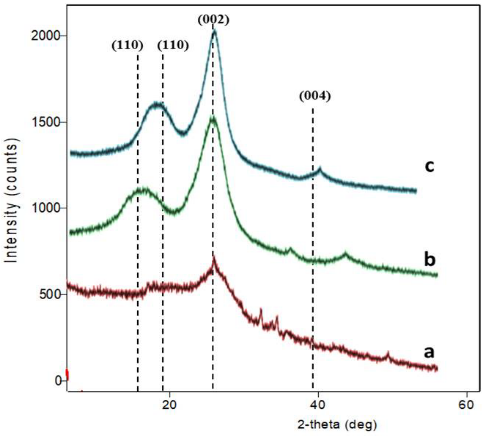

Figure 3: X-ray diffractograms of (a) RFS, (b) FSC, (c) FMCC-HCl

Table 3
Crystallinity index of RFS, FS-C and FS-MCC

Samples	Crystallinity index (%)
RFS	37
FS-C	61
FMCC-HCl	74

Thermostability

The differential scanning calorimetry (DSC) is a fundamental technique to determine the melting and thermal degradation temperatures of polymers. The DSC thermograms of RFS, FSC, and FMCC-HCl are shown in Figure 4. In all three samples, four phases of degradation occurred: (i) water evaporation, (ii) lignin degradation, (iii) hemicellulose degradation, and (iv) cellulose degradation.[51]

The first endothermic peak occurred in all thermograms from 40 °C to 150 °C which can be attributed to the evaporation of water and other volatile materials present in the samples.[52] The amorphous material absorbs more water, therefore, this peak is a little sharper in RFS. The degradation of hemicelluloses and lignin are exothermic, hence it releases more heat during pyrolysis. That is clearly observed in Table 4. ΔH values of RFS and FSC are higher than that of FMCC. Also, it can be observed from Table 4 that the degradation onset temperature (T_{onset}) and the peak temperature (T_{peak}) were higher for FMCC than for RFS and FSC, which is related to its higher thermal stability due to the high molecular ordering of the extracted MCC. The second endothermic peak is related to the degradation of cellulose, including the decarboxylation, depolymerisation and decomposition of glycosyls units.[6] FMCC-HCl and FSC start to degrade at 370.45 °C and 323.61 °C, and completely degrade at 393.77 °C and 347.07 °C, respectively. The RFS has a large amount of non-cellulosic constituents, therefore it was found to degrade at a lower temperature – of 308.58 °C and entirely degraded at 336.58 °C.

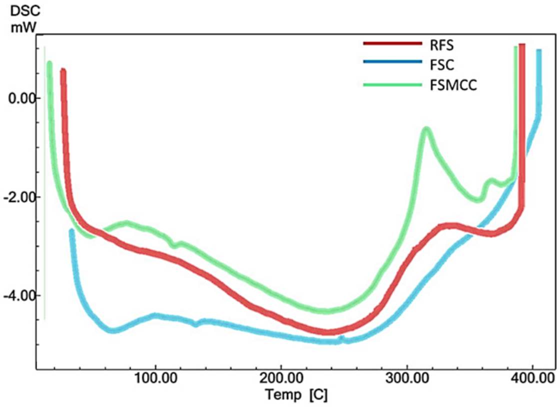

Figure 4: DSC curves of RFS, FS-C and FS-MCC

Table 4
DSC analysis data of RFS, FS-C, and FS-MCC

Samples	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)
RFS	308.58	336.54	20.52
FS-C	323.61	347.07	5.43
FMCC-HCl	370.45	393.77	3.08

Surface morphology

The morphological characteristics of RFS, FSC and FMCC-HCl samples were studied under a scanning electron microscope (SEM) and illustrated in Figure 5. Figure 5 (a) shows the SEM micrograph of RFS, revealing a compact, large, closely bundled fibre structure, with the apparently rough surface morphology, indicating that the lignin and hemicelluloses were intact at this stage. Following the alkali treatment and bleaching, the bleached fibres separated into individual fibrils, as shown in FSC (Fig. 5 (b)). The removal of pectins, waxy layers, and binding components, such as lignin and hemicelluloses, resulted in the release of individual fibres.[24] As shown for FMCC-HCl (Fig. 5 (c)), further acidic treatment disintegrated the fibres into shorter cylindrical microcrystallites. This was due to the amorphous region of cellulose being vulnerable to hydronium ions and then undergoing hydrolytic fragmentation to form smaller cellulose crystals.[19] Figure 5(c) shows the clean fibril-like appearance of FMCC-HCl due to complete elimination of non-cellulosic constituents. The size of MCC fibrils also reduced due to rearranging and realignment of cellulose polymer chains after delignification, bleaching, and acid hydrolysis. The bleaching treatment imparts a white color to the cellulose and helps in the elimination of the rest of the hemicelluloses. The acid hydrolysis converts cellulose into a more crystal structure and reduces the size of the individual fibres.[53]

Surface area and pore volume

The N_2 adsorption-desorption isotherm plot of Brunauer-Emmett-Teller (BET) analysis and the Barrett-Joyner-Halenda (BJH) plot for FMCC-HCl and FC are shown in Figure 6 (a) and (b), respectively. Table 5 describes the BET analysis data, including total surface area, total pore volume, and average pore diameter. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), FSC showed type II isotherm, which indicates a macroporous structure, with a surface area of 0.39 m^2g^{-1} and a total pore volume of 0.0024 cm^3g^{-1}.[54] The prepared

FMCC-HCl on the other hand showed type I isotherm, indicating a microporous structure with a comparatively larger surface area of 1.49 m^2g^{-1} and a smaller pore size, with the total pore volume of 0.0028 cm^3g^{-1}.[38]

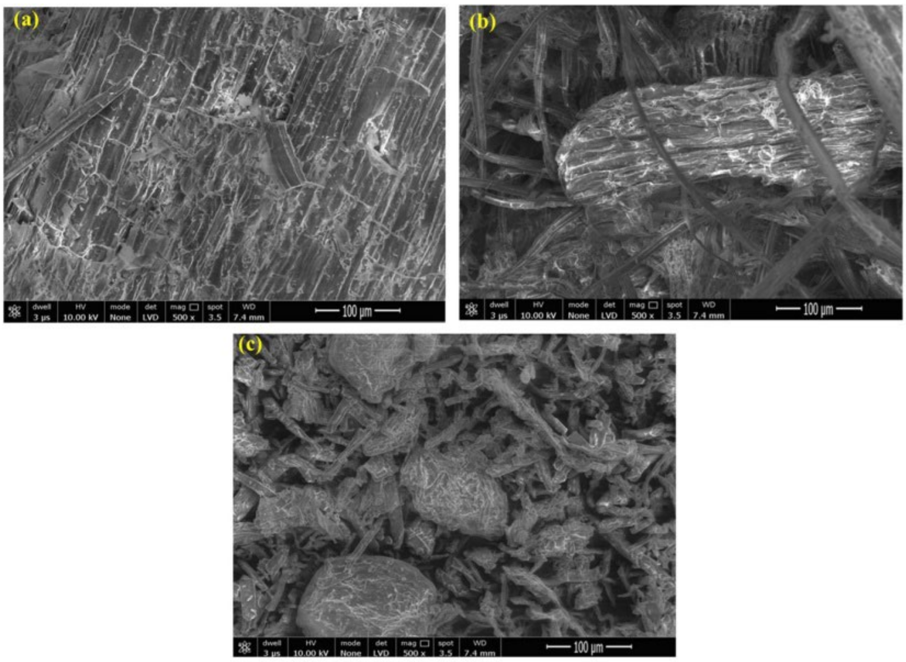

Figure 5: SEM micrographs of (a) RFS, (b) FS-C, (c) FMCC-HCl

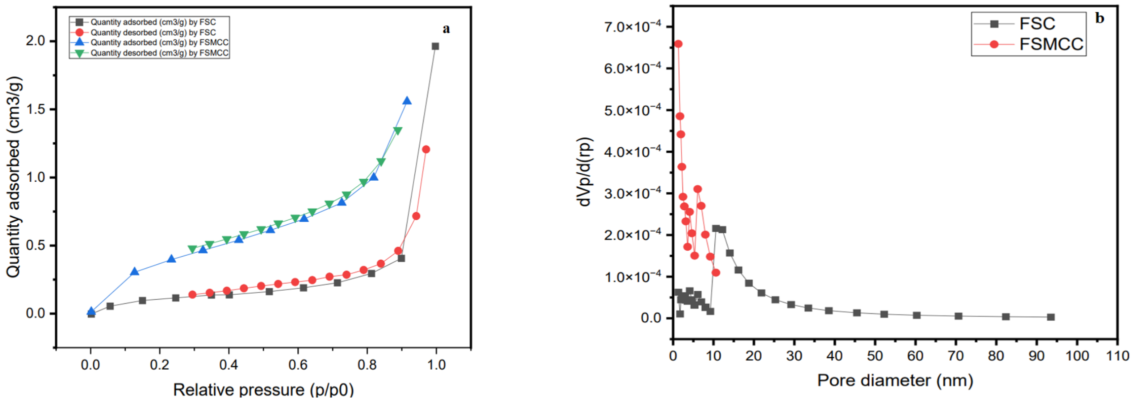

Figure 6: Adsorption isotherms (a) and pore size distribution (b) of FSC and FMCC-HCl

Table 5
BET surface area analysis of FMCC-HCl and FSC

Sample	BET plot				Langmuir plot		BJH plot		
	V_m [cm^3(STP)/g]	$a_{s,BET}$ [m^2/g]	Total pore volume [cm^3/g]	Av. pore diameter (nm)	V_m [cm^3(STP)/g]	$a_{s,Lang}$ [m^2/g]	V_p [cm^3/g]	$r_{p,peak}$ (area) (nm)	a_p [m^2/g]
FMCC-HCl	0.3445	1.4994	0.0028 (p/p_0=0.915)	6.42	0.7049	3.0681	0.0029	1.29	1.6511
FSC	0.0905	0.3939	0.0024 (p/p_0=0.990)	29.10	0.1725	0.7508	0.0025	10.61	0.4989

CONCLUSION

Microcrystalline cellulose was successfully isolated from fennel stems by using alkali, bleaching, and acid hydrolysis processes. Chemical analysis clarified that the percentage of α-cellulose increases in the prepared microcrystalline cellulose, indicating the high purity of MCC. FTIR analysis revealed the absence of characteristic peaks of lignin and hemicelluloses, pointing to their complete removal. Additionally, no damage occurred in the chemical structure of microcrystalline cellulose because of acid hydrolysis. The XRD pattern of FMCC-HCl showed that acid hydrolysis significantly increases the crystallinity index. Based on the DSC analysis, it was found that FMCC-HCl had higher thermal stability than RFS, confirming its suitability for the preparation of future polymeric composites at high temperatures. The surface micrograph taken by SEM indicates that FMCC-HCl had shorter fibre, a rough and highly porous surface after acid hydrolysis. The Brunauer–Emmett–Teller (BET) analysis reveals that the specific surface area of FMCC-HCl is greater than in FSC. The overall results evidenced that highly pure and good quality MCC was isolated from the fennel stems. Thus, such an approach may reduce the cost of commercial MCC and provide sustainable use of fennel stem waste by exploiting it as a raw material for obtaining a value-added product for various industrial scale applications.

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