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Synthesis and characterization of microcrystalline cellulose from jute stick

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Synthesis of microcrystalline cellulose from jute sticks has been studied and reported in this work. The successful removal of lignin and hemicellulose has been confirmed through Fourier Transform Infra-red spectroscopic technique, whereas WAXD technique has been used to measure the crystal size and crystallinity index. Scanning electron microscopic images depict the porous structure and agglomerate fibrous shape with hierarchical assembly of the microcrystalline cellulose produced. Higher concentration of sodium chlorite produces minimum particle size and the effective thermal degradation occurs at 340 °C. It shows negative zeta potential value, indicating the possible agglomerating tendency of the particles in water medium.

Keywords: Crystallinity index, Jute sticks, Microcrystalline cellulose, Particle size measurement

1 Introduction

Cellulose is the most abundantly available biopolymer. The chemical and mechanical degradation of cellulose leads to a low molecular weight purified and partially de-polymerized material with a degree of polymerization of less than 400 (ref 1). According to the size and shape, this microcrystalline cellulose (MCC) has a potential to be used in diverse field of applications[2-4].

Wood and cotton linter are the oldest and most commonly used raw materials for the synthesizing of MCC[5]. Now-a-days, the researchers are trying for alternative resources for the production of MCC from various cellulosic and lignocellulosic agricultural/industrial wastes. Various researchers have investigated different pre-treatment processes, viz. drying and sequential washing [6], ball milling [7], reactive extrusion at high temperature [8], cleaning and drying at sunlight and subsequently passing through fine screen [9], pyrolysis [10] and microwave based alkali pre-treatment [11] for the production of MCC. Ultrasound treatment to rupture the cellulose and hemicellulose into fractions for the production of MCC from lignocellulosic materials has also been reported [12]. Delignification process through enzymatic [13] and chemical pathway[14, 15] has also been reported in the literatures. The various chemical pre-treatment processes viz. ammonia fibre explosion[16], supercritical CO_2 treatment[17] and ionic liquids[18] have also been reported by different researchers for the synthesizing of MCC. The market demand of MCC is expected to reach 1214.4 million USD in the year of 2023 with a compound annual growth rate (CAGR) of 7%[19].

Jute is one of the major cash crops of the country and traditionally been used as packaging materials, whereas the jute stick is most commonly used as thatching for rural homes, cooking fuel, industrial fuel, fencing, etc[20-23]. Jute stick contains alpha cellulose (40.8 -47.5%) along with hemicelluloses (23 - 23.6%), lignin (22.3 - 23.5%), acetyl content (3.6-4.7%), pectin (0.5-0.7%), ash (0.6-0.8%), and fats and waxes (1.7-2.4%)[24]. The researchers have investigated alternative value-added application of jute sticks in different fields, viz. pulp and paper industries[25], bio-fuel production[26], composite making[27], activated carbon and microcrystalline cellulose[28] in order to uplift the socio-economic status of the jute cultivators and also to commercialize jute sticks in diversified fields. Keeping this in mind, the objective of the present study is to synthesize microcrystalline cellulose from jute stick through mechanical and chemical pre-treatment process. The synthesized MCC is also characterized through various instrumental techniques, viz. ATR-IR

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spectroscopic study, wide angle X-ray diffraction, scanning electron microscopy, zeta potential and particle size measurements. The weight losses at various stages of processing and final yield % have also been reported.

2 Materials and Methods

2.1 Materials

Jute sticks were collected from Nashibpur area near Hooghly district of West Bengal. Dried jute sticks were crushed in a pulverizer in order to obtain crushed particle. Laboratory reagent grade sodium hydroxide, sodium chlorite, acetic acid, hydrochloric acid (35% w/v), hydrogen peroxide (50% w/v), and sodium meta silicate were procured form Emplura Merck Life Science Pvt. Ltd, Mumbai and were used as and when required.

2.2 Methods

2.2.1 Treatment with Sodium Hydroxide

Sodium hydroxide (10% w/v) treatment was performed at 55 °C for 90 min. The dark brown extract was decanted and the highly alkaline precipitate was neutralized with acetic acid and finally washed with cold water. The precipitate was then dried in a hot air oven for 5 h at 80°C± 5°C. The dried material was taken for subsequent chemical treatment.

2.2.2 Treatment with Sodium Chlorite

Three different concentrations (0.5, 0.7 and 1.0%) of sodium chlorite were used for the removal of lignin present in the jute stick. Sodium chlorite of specified concentration was used separately at 85°C for 90 min, keeping a material-to-liquor ratio at 1:20. The treatment bath *p*H was kept at 4-5 with the addition of acetic acid. Finally, the material was dried in hot air oven for 5 h at 80°C ± 5°C.

2.2.3 Treatment with Mineral acid

After removal of lignin the residual matter was further treated with hydrochloric acid (2.5N). The treatment was carried out at 105°C for 30 min, keeping the material-to-liquor ratio at 1:30.

2.2.4 Treatment with Hydrogen Peroxide

Hydrogen peroxide (15%) along with sodium meta-silicate (7.5 %) and sodium carbonate (8%) was used for bleaching purpose. The treatment was carried out at 85°C for 30 min. The bath *p*H was maintained at ~12 and after bleaching the material was periodically washed and filtered through 120 mesh nylon bolting cloth.

2.2.5 Drying

The white paste of microcrystalline cellulose was dried at 40°C for 20 h in a hot air oven and finally crushed into powder form for further characterization.

2.3 Characterizations

2.3.1 Calculation of Weight Loss

Weight loss was calculated in accordance with the following formula:

$$\text{Weight loss (\%)} = [(W_1\text{-}W_2) / W_1] \times 100 \quad \ldots (1)$$

where W_1 is the dry weight of previous process; and W_2, the dry weight of present process.

The final yield (%) of MCC under different treatment conditions of sodium chlorite was also calculated using the following formula:

$$\text{Yield (\%)} = X_2 / X_1 \times 100 \quad \ldots (2)$$

where X_1 is the Initial weight of the jute sticks; and X_2, the final weight of the MCC produced after completion of all stages.

2.3.2 Fourier Transforms Infrared Spectroscopy

The FTIR spectra were recorded in a Perkin Elmer Spectrometer (Spectrum II) by using the attenuated total reflectance (ATR) mode.

2.3.3 Particle Size and Zeta Potential Measurements

Particle size was measured with the help of Nano ZS, Zetasizer, Nano Series, Malvern Instruments employing a 4 MW He-Ne Laser (λ= 632.8 nm) and equipped with a thermostat sample chamber. All measurements were taken at 173° scattering angle and at 298 K. Measurement of zeta potential was performed in a Zeta dip cell using a Malvern Zetasizer Model ZEN 3600.

2.3.4 TG, XRD and SEM Study

The thermo gravimetric analysis of microcrystalline cellulose samples produced from jute sticks was carried out with the help of Perkin Elmer, USA (Model: Diamond TG/DTA).

The wide angle X-ray diffraction measurement of powdered microcrystalline cellulose samples obtained from jute sticks was recorded with a PANanalytical X'Pert Pro with Cu Kα (45 kV and 30 mA) line with an incident beam wavelength of 1.54 Å. The scan range used was 10 – 60° 2θ using 0.02° step size with

30 s time per step. The crystallinity index was calculated in accordance with the following equation:

Crystallinity Index = [Area of Crystalline Peaks / Area of all Peaks (Crystalline + Amorphous)] x 100

The average crystallite size (nm) was also calculated from the following Scherrer equation[29]:

$$L = k \lambda / \beta \cos\theta \quad \ldots (3)$$

where L is the size of crystallite (nm); k, the Scherrer constant (0.90); λ, the X-ray wavelength (1.54 Å); β, the FWHM (full width half maximum) of reflection in Rad and θ, the corresponding Bragg's angle

The surface topology of microcrystalline cellulose was characterized using Hitachi S3400 scanning electron microscope with gold sputtering.

3 Results and Discussion

3.1 Physical Characterization

Weight loss during the different stages of synthesizing microcrystalline cellulose from jute sticks and final yield (%) are reported in Table 1. It is observed that the treatment with sodium hydroxide results in almost identical loss in weight for all the three samples, namely J1, J2 and J3. The loss in weight indicates the removal of hemicellulose and other added impurities present in the jute sticks. It is also noticed from Table 1 that weight loss is maximum for the application of 1% sodium chlorite (J3) and it follows an increasing trend with increase in sodium chlorite concentration (J3>J2>J1). Hypochlorous acid is more active than chlorite ion under acidic condition. It oxidizes the phenol derivatives and aldehyde groups present in lignin into its water soluble fragments[30]. The strong mineral acid is used for further de-polymerization of residual alpha cellulose and this acid hydrolysis removes the amorphous portion. Pure cellulose is disintegrated by the rupture of β-(1, 4) bonds and lowers the degree of polymerization[31-33]. After acid treatment, the total structure of jute sticks is converted into powder form and any trace of impurities present is removed during the bleaching action with hydrogen peroxide. The final yield (%) of microcrystalline cellulose varies from 25.60% to 33.40%, depending on the treatment conditions.

3.2 Infrared Spectroscopic Study

Figure 1 shows the infrared spectra of jute stick (J0) and microcrystalline cellulose produced through different concentrations of sodium chlorite, i.e. J1, J2 and J3. The broad absorption peak at 1238.40 cm^{-1} corresponds to C-O stretching of esters, vinyl ether linkages and alkyl aryl ether, which indicates the presence of lignin and its derivative in J0. This peak is absent in other three samples (J1, J2 and J3), indicating the successful removal of lignin. The absorption bands at 1504.88 cm^{-1} and 1372.24 cm^{-1} are due to the C=C stretching of aromatic rings present in lignin and C-H asymmetric deformation[34]. These are also absent in the treated samples and signifies the successful removal of impurities from jute sticks.

The broad absorption bands at 3330-3360 cm^{-1} and 2896.19 cm^{-1} noticed in all spectra are due to the

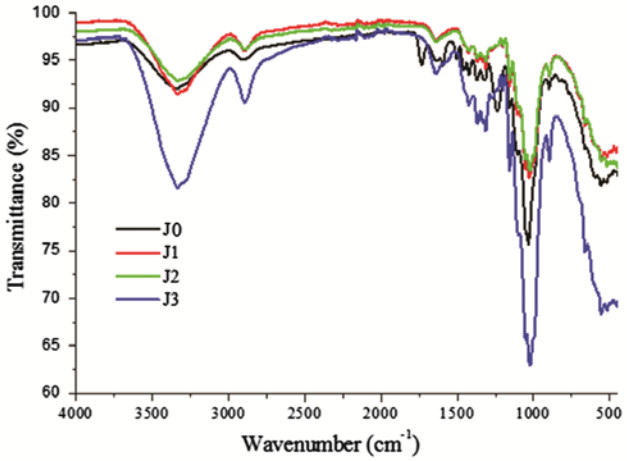

Fig. 1 — Infrared spectra of raw jute sticks (J0) and samples treated with 0.5% (J1), 0.7% (J2) and 1% (J3) sodium chlorite respectively

Table 1 — Weight loss in different stages of processing and final yield

$NaClO_2$, %	Jute sticks g	Treatment with sodium hydroxide		Treatment with sodium chlorite		Treatment with hydrochloric acid		Treatment with hydrogen peroxide		Final yield, %
		Actual weight g	Weight loss %	Actual weight g	Weight loss %	Actual weight g	Weight loss %	Actual weight g	Weight loss %	
0.5% (J1)	20	14.5		10.40	28.30	7.10	31.7	6.67	6	33.4
0.7% (J2)	20	14.5	27.5	9.2	36.56	5.90	35.8	5.62	4.7	28.1
1.0% (J3)	20	14.5		8.6	40.69	5.33	37.8	5.12	4	25.6

stretching of - OH groups and C-H stretching vibration respectively[35]. This clearly indicates the presence of cellulose in all the materials. The intramolecular hydrogen bonding for 2-OH…O-6 and 3-OH…O-5 and intermolecular hydrogen bonding for 6-OH…O-3 appears at 3450-3410 cm^{-1}, 3333.20 cm^{-1}, and 3331-3215 cm^{-1} respectively[36, 37]. The hydrogen bond energy and the bond distance for several -OH stretching bands is also calculated[38].

Table 2 shows the bond energy value of raw jute sticks (J0) and microcrystalline cellulose synthesized through specified concentration of sodium chlorite. It is observed from the table that the bond energy for J0 is lower as compared to the microcrystalline cellulose produced from the jute sticks. It suggests the higher interaction between intramolecular cellulose chains of synthesized MCC from jute sticks [39].

There is a variation in peak height near 3330 cm^{-1} for the samples produced through different concentrations of sodium chlorite as compared to raw jute stick (J0). This apparently indicates the presence of more number of hydrogen bonds in the microcrystalline cellulose[40].

3.3 Particle Size and Zeta Potential

Figure 2 shows the average particle size of the MCC synthesized from jute sticks under three different dose levels of sodium chlorite. Increase in sodium chlorite concentration results in lowering of average particle size. The lower particle size in case of J3 may be attributed to the higher concentration of sodium chlorite used as delignifying agent followed by acid hydrolysis with strong mineral acid.

The negative zeta potential value for all the samples follows the order J3 (- 19.3 mV) > J2 (- 18.2 mV) > J1 (- 17.5 mV). The negative zeta potential values indicate a stable suspension and possible agglomerating tendency of the particles in water medium. Among the different concentrations of sodium chlorite as delignifying agent, J3 produces best results in respect to particle size and zeta potential. It is also found that the hydration tendency of J3 is also higher as compared to J1 and J2.

Table 2 — Hydrogen bond energy and bond distance

Sample	Wave number, cm^{-1}	Bond energy, kJ	Bond distance, Å
J0	3339.78	19.25	2.91
J1	3335.26	19.53	2.91
J2	3337.19	19.51	2.91
J3	3335.14	19.53	2.91

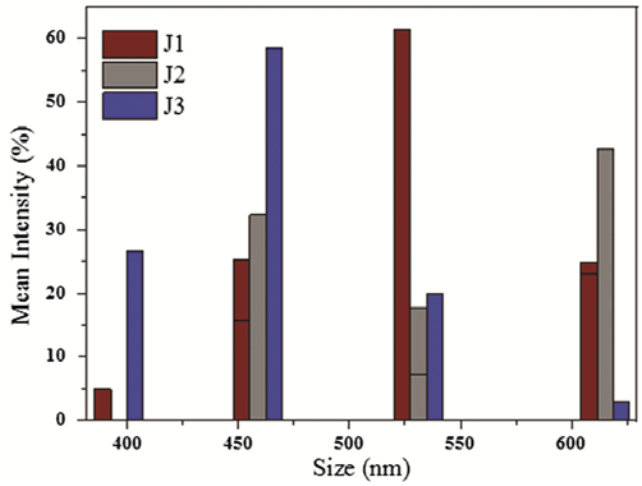

Fig. 2 — Particle size of jute sticks treated with 0.5% (J1), 0.7% (J2) and 1.0 % (J3) sodium chlorite concentration

3.4 Wide Angle X-ray Diffraction

Figure 3 shows the X-ray diffractograms (XRD) of raw jute sticks (J0) and microcrystalline cellulose synthesised through 0.5%, 0.7% and 1.0% sodium chlorite as delignifying agent. In all the cases, the pattern shows a distinct semi crystalline material with an amorphous broad hump (at 2θ = 14-15.5°) and crystalline sharp peak (at 2θ = 22.5°) which represents the cellulose crystallographic plane. The average calculated value of crystallinity Index is around 60% in all the treated samples. It may be due to constant acid concentration used for hydrolysis. The crystal size as calculated by using Scherrer equation is approximately 6.9 nm, which is very much similar to the MCC produced from rice hulls (5.77 nm), bean

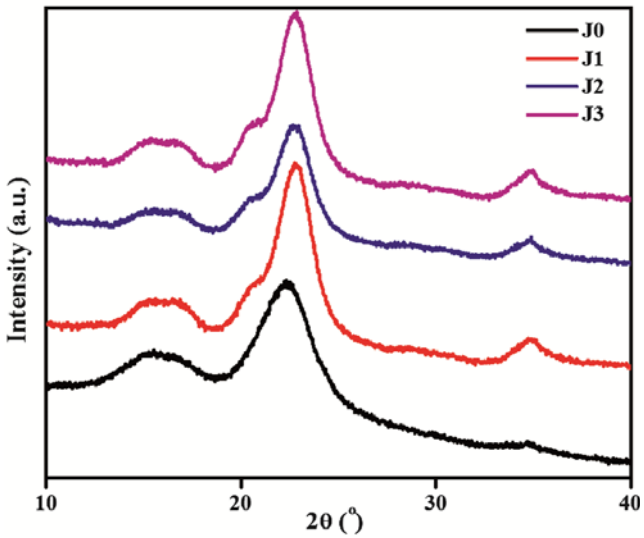

Fig. 3 — Wide angle X-ray diffraction pattern of raw jute sticks (J0) and microcrystalline cellulose produced through 0.5% (J1), 0.7% (J2) and 1.0% (J3) sodium chlorite as delignifying agent

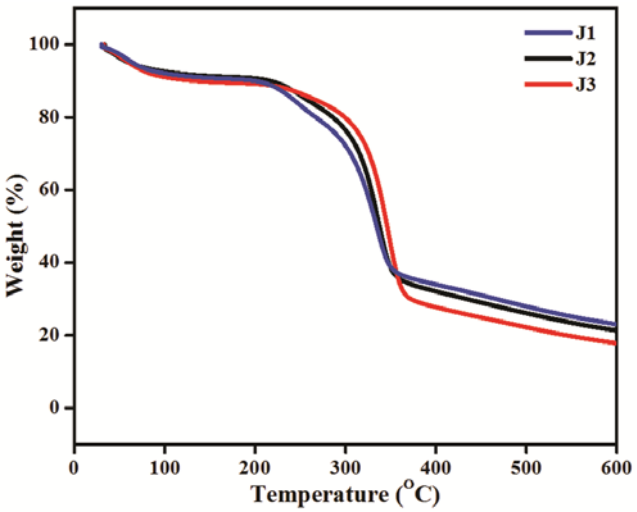

Fig. 4 — TGA curve of microcrystalline cellulose from jute sticks with 0.5% (J1), 0.7% (J2), 1% (J3) of sodium chlorite concentration

hulls (9.07) and the commercial MCC made by Avicel 101 (7.94 nm) [41].

3.5 Thermo Gravimetric Analysis (TGA)

Figure 4 shows the thermal degradation pattern of microcrystalline cellulose produced from jute sticks at different concentrations (0.5, 0.7 and 1.0%) of sodium chlorite as delignifying agent. In all the cases, effective thermal degradation occurs at 340°C temperature. The cleavage of glucosidic linkage in cellulose leads to the formation of water, carbon di-oxide, alkenes and others hydrocarbon derivatives at the temperature range 230 -370°C. This correlates with the value of decomposition peak for cellulose as observed by different researchers[42, 43].

3.6 Scanning Electron Microscopic Analysis

The SEM images (Fig. 5) of microcrystalline cellulose confirm its morphological structure. Figures 5(a) and (b) shows the compact and solid surface of untreated jute sticks (J0) at different magnifications. Figures 5(c) and (d) describe the cleaned rough surface of MCC produced when 0.5 % sodium chlorite (J1) is used as delignifying agent. Figures 5(e) and (f) indicate the surface coarseness of the rod shaped MCC (J2). Figures 5(g) and (h) exhibit the porous structure and agglomerate fibrous structure with hierarchical assembly (J3). These morphological observations indicate the strong mechanical properties of microcrystalline cellulose obtained from jute sticks, which corroborates to the findings of other researchers [44, 45].

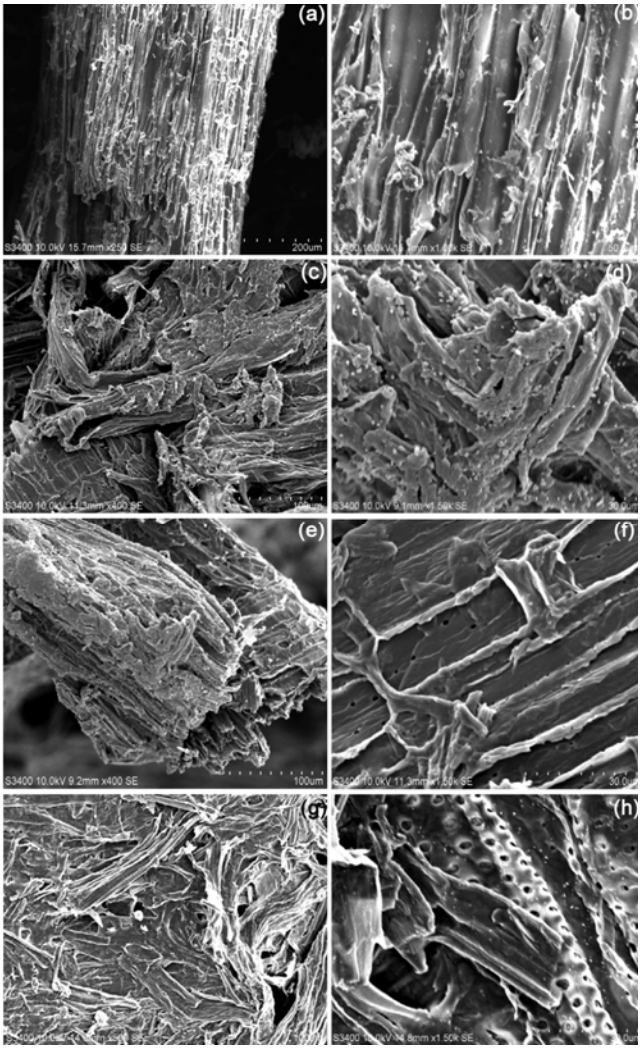

Fig. 5 — SEM images of (a) and (b) jute sticks (J0), and microcrystalline cellulose obtained after treating with three different concentrations (c) and (d) 0.5 % [J1], (e) and (f) 0.7% [J2] and (g) and (h) 1.0% [J3] of sodium chlorite at different magnifications

4 Conclusion

Jute sticks can be used as the raw materials for producing microcrystalline cellulose. The higher concentration of sodium chlorite produces optimum results in terms of particle size and % yield. The infrared spectroscopic analysis reveals the effectiveness of the process to eliminate lignin and other impurities present in jute stick. The microcrystalline cellulose synthesized from jute sticks shows negative zeta potential value, indicating stable suspension along with possible agglomerating tendency of the particles in water medium. The MCC produced shows the crystallinity index of around 60% with crystal size of 6.9 nm. SEM images exhibit the

porous structure with agglomerate fibrous shape, which may attribute desirable mechanical properties of synthesised MCC from jute sticks. Availability of jute stick at lower price in local areas can be explored for the production of microcrystalline cellulose.

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