Degumming of Hemp Fibers Using Combined Microwave Energy and Deep Eutectic Solvent Treatment

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Abstract

Hemp bast fibers were degummed using combined microwave energy (MWE) and deep eutectic solvent (DES) to generate pure hemp cellulose fibers for potential textile applications. The properties of the obtained fibers were investigated and compared with those from the traditional alkali-based process using several analytical techniques. Results revealed that hemp fiber surface underwent dramatic structural disruption during the pretreatment, due to the removal of “gummy” compounds (i.e., lignin, pectin, oil, and wax) and amorphous cellulose. Ultraviolet (UV) protection factor (UPF) of DES-treated fibers with 1:20 fiber-DES ratio (i.e., 183.67) were significantly higher than those from the traditional alkali-treated (140.75) and untreated raw hemp fibers (127.47). The treated fibers also had higher thermal stability. Chemical composition analysis showed that the cellulose content in the treated fiber samples increased to 49.95% which was comparable with the cellulose content of the alkali-treated fibers (49.49%). The study demonstrates a potentially effective, less time-consuming, and environmentally sustainable protocol for manufacturing purified hemp cellulose fibers using combined MWE-DES treatment.

Introduction

Hemp has garnered great interest due to its biodegradability, low-cost, and fast-growing capability under mild and harsh weather conditions throughout the world (Dhondt 2020). Long hemp bast fibers from hemp stalk have been used for a myriad of applications such as textiles, paper, and biodegradable composites (Wang et al. 2020). Chemical composition of hemp bast consists of cellulose, lignin, hemicellulose, and gums including pectin, oil, wax, minerals (Liu et al. 2017; Keiller et al. 2021), and other non-cellulosic components. Gums in natural fibers are complex carbohydrate polymers with long sugar chains including hydroxyproline proteins, resins, and other compounds that can be soluble, partly soluble, or insoluble. Lignin is a complex polymer of aromatic and aliphatic components of three monolignols (hydroxycinnamyl) such as coniferyl alcohol, sinapyl alcohol, and \( \rho \)-coumaryl alcohol. The presence of the gum and lignin in hemp fibers leads to difficulties in further textile processing of hemp fibers such as spinning, weaving, dyeing, and other finishing processes. Thus, the degumming (i.e., removing gums, lignin, and other non-cellulosic components) of hemp fibers is a crucial step for the effective utilization of the fibers.

There are many methods of hemp fiber degumming including chemical (Zhu et al. 2021), mechanical (Liu et al. 2017), thermal (Gedik and Avinc 2020), water retting, high energy irradiation (Stelescu et al. 2020), and other methods. Studies have been done on several chemicals and strategies including alkali treatment, acetylation, bleaching, salinization, benzoylation, and other treatments using organic and inorganic acids, peroxide, chelating agents, anhydrides, sodium chlorite, and sodium sulfite (Kabir et al. 2020; Menghini et al. 2021). Even though chemical treatments are able to make the finest quality of fibers, they can cause several negative impacts on the environment by generating a high amount of effluent and requiring high energy inputs, leading to increased production cost. Replacing chemical treatments with other biological treatments alone cannot produce suitable individual hemp fibers as
hemp raw fiber contains only about 57-77% cellulosic compounds (Stevulova et al. 2014). Thus, there is a need to develop an environmentally friendly and cost-effective degumming process.

Over the last few decades, ionic liquids (ILs) have exhibited promising properties for treating lignocellulosic materials. However, certain properties of ILs including toxicity, high cost, and destructive structural impact on cellulose have limited their widespread use. Deep eutectic solvent (DES) is an alternative ionic liquid that is largely biodegradable (Abbott et al. 2004). DESs can be synthesized by the combination of two or three components, where a certain mix of hydrogen bond acceptors (HBA, e.g., quaternary ammonium salts, choline derivatives, organic acids) and hydrogen bond donors (HBD, e.g., amides, polyols, and carboxylic acids) is used. The eutectic solution consists of nonsymmetric and large ions with low lattice energy and has a melting point that is significantly lower than the melting points of the individual components in the mixture. The charge delocalization occurs through the formation of hydrogen bonds, leading to the suppression of melting points in the eutectic mixture compared with these of individual components. One of the main advantages of DES is that DES offers similar physiochemical properties to ILs while being more sustainable, cheaper, and having lower toxicity compared with ILs. Additionally, the recyclable and reusable traits of DES have made it more attractive for the treatment of biomass. It has been reported that DES can extract lignin without the alteration of the cellulosic structure of lignocellulosic materials (Tan, Chua, and Ngoh 2020). DES has been utilized in several sectors such as delignification, biodiesel production, and sugar recovery. DES has also been employed in the surface treatment of lignocellulosic materials, including ramie (Yu et al. 2020), kenaf bast (Nie et al. 2020), and apocynum bast (Song et al. 2019). It has been found that DES treatment has a comparable degumming effect to that of traditional degumming methods (alkali, silane, and bleaching treatment).

Traditional heating systems for the degumming process including steam, gas, and electric energy sources have several disadvantages such as longer treatment time to achieve the desired temperature and process inefficiency, and excessive cost. Recently, microwave energy (MWE) heating has gained a lot of attention as a pretreatment process of lignocellulosic materials due to its efficiency, low hazards, and reduced treatment time. MWE heating is also able to separate fibers from the cell walls of hemp stem (Sun et al. 2019). Microwave is electromagnetic radiation in the spectrum between 300 and $3 \times 10^5$ MHz, a region that lies between radio frequencies and infrared, and corresponds to wavelengths of 1 cm to 1 m (Motasemi and Ani 2012). Due to the thermal effects of MWE, a structural change occurs in the lignocellulosic materials in the presence of a solvent as the dipole molecules of the fibers are intended to align themselves with the applied electric field direction of the microwave. Due to the electromagnetic treatment of microwave, the fibers can be acted as a non-homogeneous material that allow the fibers to increase polarity, hence fiber material can easily absorb the MWE through the formation of hotspots within the fiber. Nair et al. (Nair et al. 2015) produced high quality fibers using a microwave-assisted hot water degumming, evidenced by the Near Infrared (NIR) analysis of the degummed hemp fibers. The degumming performance of natural fibers mainly hinges upon the effective breakage of hydrogen bonds of hemicellulose and lignin. Therefore, it is hypothesized that the combined MWE-DES treatment of hemp
fibers can be a promising alternative to degum the hemp bast fiber for attaining high-quality hemp cellulose fibers with improved mechanical and thermal properties.

The objective of this study was to use combined MWE-DES treatment for degumming hemp bast fibers to produce purified hemp cellulose fibers for the subsequent textile, nanocellulose, and composite manufacturing. DES made of choline chloride and urea was used to treat hemp fibers. Scanning electron microscopy (SEM), Fourier Transform Infrared (FT-IR), Near-Infrared Magnetic Resonance (NMR), and X-ray Diffraction (XRD) techniques were used to evaluate the fiber surface morphology and physiochemical properties. Thermal property characterization of fibers was performed by Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC).

### Experimental Section

#### MATERIALS

Raw hemp bast fibers were obtained from a local supplier. The fibers contained a small percentage of woody core (hurd). Choline chloride (pure > 98%) was purchased from TCI America (Portland, OR, US), urea (crystallized) was procured from VWR BDH Chemicals (Radnor, PA, US), sodium sulfate (anhydrous) was acquired from VWR Life Science (Solon, Ohio, US), sodium metasilicate was purchased from BTC Beantown Chemicals (Hudson, NH, US), sodium hydroxide (ACS-grade pellets) was bought from Fisher Chemical (Fair Lawn, NJ, US), sodium polyphosphate (pure) was purchased from ACROS Organics (Fair Lawn, NJ, US), and hydrogen peroxide - 30% (aqueous solution of ACS reagent grade) was supplied by J.T. Baker (Radnor, PA, US).

#### DEGUMMING PROCESS

The woody core (hurd) from the raw hemp fibers was removed manually using a small carding machine. The processed bast fibers were stored in the laboratory condition before the degumming experiments.

**Traditional alkali degumming.** Cleaned raw hemp samples were cooked at 90°C for one hour with a 1% NaOH solution in an oil bath and the solid-liquid ratio was 1:20 (volume/weight). After boiling, the hemp fibers were washed with tap water five times to achieve neutrality. The recipe for the alkali degumming includes 1% sodium hydroxide (NaOH), 3% hydrogen peroxide (H₂O₂), 3% sodium polyphosphate (NaPO₃), 2% sodium sulfate anhydrous (Na₂SO₄), 3% sodium metasilicate (NaSiO₃), and 3% urea (CH₄N₂O) (Jiang et al. 2018). The fiber-liquid ratio of the alkali degumming was 1:20 and all the chemicals were weighed according to the weight/volume ratio. After cooking with the abovementioned recipe for one hour, the hemp fibers were removed and washed with tap-water five times to achieve neutrality and the fibers were slowly dried in an oven at 60°C. The dried fibers were kept for further characterizations.

**Combined MWE - DES degumming.** Choline chloride was used as a hydrogen bond acceptor and urea was used as a hydrogen bond donor. DES (Figure 1) was synthesized from the mixture of choline chloride and
urea at a molar ratio of 1:2. The mixture was heated at 80°C and stirred magnetically for about 2 hours in the oil bath until a transparent and homogenous solution was obtained. The hurd-free hemp fiber samples were submerged into the DES solution in a 90 ml Teflon vessel. The microwave extraction system (model: Ethos X, Milestone Inc, Shelton, CT, US) was used for the degumming of fiber samples at 1:10 and 1:20 fiber-DES ratio for 60 min and 90 min, respectively. The power and stirring levels of the microwave extraction system were 1000kW and 24%, respectively. After degumming (Figure 2), fibers were washed with tap water, oven-dried, and kept for further characterizations. Some of the MWE-DES treated hemp fibers were further subjected to mild alkali treatment. After the alkali treatment, the obtained fibers were washed with tap water and oven-dried. Raw and treated hemp fibers are designated as Raw (raw hemp fibers), A (alkali-treated fibers), B (MWE-DES treated fibers at a solid-liquid ratio of 1:10), C (MWE-DES predegummed at a solid-liquid ratio of 1:10 and alkali-treated fibers), D (MWE-DES treated fibers at a solid-liquid ratio of 1:20), and E (MWE-DES predegummed at a solid-liquid ratio of 1:20 and alkali-treated fibers).

CHARACTERIZATION

Fiber surface morphology. Hemp fiber surface (both raw and degummed) morphology was investigated by using a high-performance electron microscope (Model-JSM-6610 LV SEM, JEOL, Japan) in a high vacuum condition at an accelerated voltage of 5kV. Before scanning, the fiber samples were cut into small pieces and coated with a thin layer of gold using an EMS550X sputter coater.

Fourier transform infrared analysis (FT-IR). Fourier Transform Infrared analysis (FT-IR) of hemp fibers (both raw and degummed) was performed to identify the presence of free functional groups. FT-IR spectra were obtained using a Bruker Alpha & Tensor 27 FT-IR spectrophotometer and OPUS software. The operating conditions were as follows: 32 scans per sample, resolution of 4 cm⁻¹, with a wavelength range of 400-4000 cm⁻¹.

X-ray diffraction (XRD) analysis. Hemp powdered fibers (both raw and degummed) were analyzed by X-ray diffraction using a PANalytical Empyrean X-ray Diffractometer (Malvern, UK) equipped with the PreFIX modules (Fast interchangeable X-ray). The diffractometer was operated at 40mA and 40kV with the Ka -1 wavelength of 1.540598, Ka -2 wavelength of 1.54426, Cu-anode material, scan range of 5-50, and scan step size of 0.0131303 to get the diffraction patterns of both raw and degummed hemp fibers. The crystallinity index of raw and degummed hemp fibers was analyzed using the Segal equation from the X-ray diffraction spectra (Segal et al. 1959).

\[
CrI \% = \frac{I_{200}-I_{am}}{I_{200}} \times 100\%
\]  

\[I_{200}\] represents the maximum intensity of the lattice peak of 2q angle at 22.6 degrees, which is imputed to the crystalline region. \[I_{am}\] denotes the intensity of 2q angle at 18 degrees, concerning the amorphous
region of cellulose. The average crystallite size from the XRD diffractograms was calculated by using the Scherrer equation (Scherrer 1912).

\[ d = \frac{K\lambda}{\beta\cos\theta} \]  

where \( d \) = average crystallite size in nm, \( K \) = Scherrer constant = 0.94 for spherical crystallites, \( \cos\theta \) = X-ray wavelength, \( Cu \) \( Ka \) = 1.5406 angstrom, \( b \) = Line broadening at FWHM (Full-Width-Half-Maximum) in radians, and \( \theta \) = Bragg's angle in degrees, which is half of \( 2\theta \).

**Chemical composition analysis.** The Solid-State NMR test of both treated and untreated hemp fibers was carried out using a 3-channel Bruker AV-400 (Bruker BioSpin, Billerica, MA, US) equipped with the 400 MHz spectrophotometer. These solid-state instruments were fitted with Z-axis gradients. The conditions for one-directional (1D) cross-polarization magic angle (CP/MAS\(^{13}\)C NMR) were as follows: MAS rate-10kHz, 4096 Scans, relaxation delay-2s, and CP contact time-2ms. NMR data were analyzed and processed with the Topspin Software (version-2.1) (Bruker), Origin Pro (2021 version), and dmt (NMR@CEMHTI) software. The obtained data from Topspin and Origin software were processed by utilizing Gaussian/Lorentzian models through dmt software to obtain chemical compositions of both raw and degummed hemp fibers.

**Thermogravimetric analysis (TGA).** Thermogravimetric analysis was performed for both raw and degummed hemp fibers in a nitrogen atmosphere with a flow of 40ml/min by using a TG analyzer (Model-Q50, TA Instruments Inc., New Castle, DE, US). The heating rate was 10°C/min up to 600°C at room temperature. All TG samples were about 20 mg and kept in the platinum crucible. TG and derivative TG curves were obtained as a function of weight and temperature to investigate the thermal degradation of hemp fibers.

**Differential scanning calorimetry (DSC) analysis.** DSC measurement was conducted with a Q10 DSC (TA Instruments Inc., New Castle, DE, USA) and operated at a 40 ml/min sample purge flow rate under a nitrogen atmosphere. Fiber samples were heated from 30°C to 540°C at a heating rate of 20°C/min. All DSC samples were about 5 mg.

**UV-Vis spectrophotometry and UV shielding property analysis.** A UV-vis spectrophotometer (Evolution 350, Thermo Scientific, Waltham, MA, US) was used to investigate the UV-shielding performance of both raw and degummed fibers according to the slightly modified Australia/New Zealand (AS/NZS 4399:2017) standard (AS/NZS 2017). Sample fiber films of treated and untreated hemp fibers were made at 100°C using a small hot press. The obtained fiber films were scanned with the spectrophotometer equipped with an integrating sphere at a wavelength range of 290-400nm and a slit bandwidth of 1 nm. Transmittance was recorded at 5 nm intervals. The UV protection factor (UPF) is regarded as the protection efficiency of fibers or fabric from UV radiation. A higher or lower UPF value is defined as fibers or fabric's higher or lower protection level from the UV radiation, respectively. UPF was calculated as
where $E_\lambda$ = CIE Erythemal spectral effectiveness, $S_\lambda$ = Solar spectral irradiance for a typical summer day, $T_\lambda$ = Spectral transmittance of fibers, $\Delta \lambda$ = Wavelength Step. The UPF results of various samples were discussed according to the Australia/New Zealand standard (AS/NZS 4399:2017).

Results
Hemp fiber morphology. The SEM images revealed the surface morphology and degumming effect of treated and untreated hemp fibers. The raw hemp fibers (Raw) (Figure 3a and 3b) containing lignin, hemicellulose, oil, waxes, and pectin show a rough surface. The alkali-treated hemp fibers (A) had a noticeably clear fiber surface, due to the removal of gum from the fiber structure. The clear and smooth surface of alkali-treated fibers (Figure 3c, d) revealed good individual fibers with the whitened effect, which was due to the use of NaOH and H$_2$O$_2$ (for removing lignin and destruction of inherent chromophores present in the raw hemp fibers). Furthermore, the aqueous solution of hydrogen peroxide acts as a eutectic mixture therefore the depression of boiling point accelerates the degumming process of hemp fibers with a low process temperature in the alkaline-peroxide solution (Kačer et al. 2012). As the electron delocalization occurred in the conjugated double bonds of fibers allow to absorb visible light, therefore, a whitening effect can be found on the degummed fibers. As shown in Figure 3e, f, i, and j, MWE-DES treated fibers (B and D) showed an exceptionally smooth and clear surface. Even though DES-treated fiber at 1:10 ratio (Figure 3e) had a comparatively less clear surface, this might suggest the presence of low content of gummy materials. However, after increasing the microwave heating temperature and DES-fiber ratio (SEM micrographs in Figure 3i and j of DES-treatment at 1:20 DES–fiber ratio), the hemp fibers had a clean surface with a white glowing appearance which was comparable with alkali-treated fiber surfaces. MWE-DES treated fibers (D) (Figures 3i and j) had very few cracks and voids even after increasing the process temperature and time up to 120°C and 1.5 hours; this might be caused due to the uniform dispersion of microwave heating throughout the hemp fiber structure and low freezing temperature of DES (12°C). On the other hand, subsequent alkali treatment of MWE-DES-treated fibers (C and E) revealed some pits and cracks (Figure 3g, h, k, and l) in the fiber surface due to the direct attack of alkali into the cellulose of the fiber structure since DES treatment removed most of the gummy matters. In addition, lignin is strongly linked by the hydrogen bonds and formed lignin-carbohydrate complexes. However, these strong hydrogen bonds can be weakened due to the formation of competing hydrogen bonds between the hydroxyl groups of lignin-carbohydrate complexes and the chloride ions of the DES network; thus, lignin could be removed from the MWE-DES treated fiber structures. However, the H$^+$ protons (from the hydrogen bond donor of DES) can selectively cleave the ester and/or ether linkages of lignin-carbohydrate complexes without the destruction of C-C bonds of cellulose, removing hemicellulose and lignin from the fiber structure.
Surface functional groups of hemp fibers. FT-IR spectra were used to investigate the presence of the functional groups and the degumming effectiveness of both raw and degummed hemp fibers (Figure 4). The band of FT-IR spectra at 894 cm\(^{-1}\) is ascribed to the \(\beta\) (1-4) glycosidic bonds of cellulose in the polysaccharides (Kalisz et al. 2021). The symmetric vibration in the plane of C-O-C glycosidic linkages appeared at the band of 894 cm\(^{-1}\) for all the hemp samples as seen in Figure 4. It signifies that the structure of cellulose has undergone little change in all the treated hemp fibers. The functional group assignment of FT-IR spectra wavenumbers of raw and degummed hemp fibers is represented in Table 1. The stretching of ester groups and carbonyl groups (C=O) of hemicellulose and lignin were recognized at the band of 1741 cm\(^{-1}\) (Liu et al. 2007). The disappearance of the peak at 1741 cm\(^{-1}\) for all the degummed hemp fibers indicted the removal of hemicellulose from the fiber structure (Stevulova et al. 2014). The characteristic peak of lignin was observed at the band of 1624 cm\(^{-1}\) (C=C stretching of the aromatic ring). However, the peak was weakened after alkali treatment, stretched and shifted a little bit for the DES treatment at 1:10 fiber-DES ratio, and gradually reduced and disappeared after the DES treatment at 1:20 fiber-DES ratio, which was a clear indication of the removal of gum. The bending of methylene carbons (CH\(_2\)) of lignin and hydroxyl groups (OH) in-plane bending were observed at the 1424 cm\(^{-1}\) and 1376 cm\(^{-1}\) bands, respectively. Those two peaks appeared as straight and stretched in the
treated fibers. The changes in the characteristic vibration peaks at 2916 cm\(^{-1}\) and 1741 cm\(^{-1}\) indicated that chemical modification had occurred in the DES-treated fibers. The absence of the peak at 2831 cm\(^{-1}\) in the DES-treated samples signaled the removal of oil and waxes from the hemp fibers after degumming, except for the sample B. The vibration absorption peak of hydroxyl groups at the band of 3316 cm\(^{-1}\) was getting stronger and stretched for both alkali and MWE-DES treated samples due to the reaction that occurred between DES and fiber (for the DES-treated fibers), and sodium hydroxide and fiber (for the alkali treatment).

Crystallinity of hemp fibers. Figure 5a represents the XRD spectra of treated and untreated hemp fibers. The peaks at 14.6° and 16.4° were assigned to the characteristic peak of cellulose-I and appeared as a wide peak at raw hemp XRD spectrum due to the presence of lignin, pectin, and hemicellulose (Perel 1990). The peaks at 14.6°, 16.4°, 22.6°, and 34.8° corresponded to the crystalline phase of hemp fibers in planes 110, 1 1 0, 200, and 400, respectively (Hosseinmardi et al. 2018). The peaks of the crystalline phases were intensified and strengthened after alkali and DES treatment with the strongest peak for the DES treatment at 1:20 fiber-DES ratio. This indicates the impact of DES treatment on the orientation of crystalline cellulose. In a similar fashion, the intensity of the amorphous region peak at 18° was decreased as was expected after the DES treatment at a higher ratio and temperature. The two peaks at 14.6° and 16.4° gradually became closer for the alkali-treated and MWE-DES-treated samples (as the solid: liquid ratio and time-temperature of the degumming process increased), signifying the increased crystalline lattice and the removal of lignin, pectin, and hemicellulose. The crystallinity % and crystallite size data of both raw and degummed and hemp fibers are shown in Figure 5b and c. DES treatment enables the cellulose chains to be tightened and strengthened found in the literature (Besbes, Vilar, and Boufi 2011). The crystallinity % of the DES-treated fibers was increased as compared to that of raw hemp fiber (Raw). It was an obvious indication of the removal of non-cellulosic components (non-crystalline elements) from the hemp fiber structure. It was reported from previous research that the removal of gummy materials facilitates the cellulose chains to be relaxed (increased stress relaxation) (Viscusi, Barra, and Gorrasi 2020). Therefore, microfibrils of the cellulosic components might get rearranged; the polymeric chain and surface morphology after alkali or DES treatment could be altered due to the reaction of Na\(^+\) and hydroxyl groups of fibers (for alkali-treated), and cationic component (choline\(^+\)) of the DES network and hydroxyl groups of fibers (for MWE-DES treated fibers).

Chemical compositions of hemp fibers. CP-MAS/\(^{13}\)C-NMR is an effective technique to illustrate the structure and chemical composition of polymeric materials. The peaks in the 60-110 ppm (Figure 6c) range revealed the solid-state NMR spectra of cellulose and hemicellulose. The chemical shift at 105 ppm corresponds to the cellulose C\(_1\) carbons, and the up-field shoulder peak at 103 ppm is attributed to the hemicellulose or xylan carbons (Terrett et al. 2019). The C\(_4\) carbon of cellulose showed a peak in the spectra at 89 ppm, which is ascribed to the carbons of the crystalline region. The peak of 72 ppm to 75 ppm corresponds to the cellulose carbons superimposed to the nearby xylan peaks. Carbon C\(_6\) of
crystalline and amorphous cellulose has a similar type of observations and interpretations at 63 ppm to 65 ppm by Bonatti et al. (Bonatti et al. 2004). Carbonyl and methoxy groups of lignin showed peaks at 174 ppm and 56 ppm, respectively (Moussa et al. 2020). As shown in Figure 6b,d, raw hemp fiber (Raw) had a broad peak at 174 ppm, and 56 ppm that gradually became absent in the Microwave-DES treated fibers (as the temperature, time, and solid-liquid ratio increased) and alkali-treated fibers. It was a clear indication of the removal of lignin and breakage of hemicellulose to be turned into glucose molecules and contributed to increased crystallinity and chemical composition rate of cellulose in the fiber structure. This phenomenon has a closer agreement with the XRD spectra (Figure 5a) of the raw and degummed hemp fibers. In addition, the broad peak at 21 ppm and the small peak at 32 ppm in the raw hemp are assigned to the methyl groups and methylene carbons of lignin and xylan, respectively. However, after DES treatment, those peaks were nowhere to be found (Figure 6b). The disappearance of the peaks is indicative of the removal of gummy compounds in the treated fibers.

Lignin, a complex biopolymer can be derived from the polymerization of phenyl propane monomers, synapsyl alcohol, coniferyl alcohol, and p-coumaryl alcohol (Hansen et al. 2016). These carbons of monolignol units exist in the aromatic lignin region as amino acid groups in the raw hemp fibers, disappearing after the alkali and DES treatment (Figure 6d). The signals in the NMR spectra of raw hemp fibers at 21 ppm and 174 ppm are the consequence of agglomeration and interaction of hemicellulose and methyl moieties associated with acetyl groups (Simmons et al. 2016). The signal at 81 ppm of C₄ is also generated due to the interaction of cellulose and xylan present in the raw hemp fibers. This wide-ranging signal disappeared after DES and alkali treatment. This is caused by the removal of hemicellulose and lignin from the fiber structure, which is also supported by the previous literature (Hosseinmardi et al. 2018). It is possible to find the carbon ratios which existed in the lignin structure by an integration of the area between 110 ppm-160 ppm (Fu et al. 2015). According to the literature, the chemical shift at 64 ppm could be assigned to the C₅ of xylan or hemicellulose (Simmons et al. 2016), and this signal was flattened after DES and alkali treatment, indicating the removal of hemicellulose. A similar explanation can be used for the NMR band at 84 ppm. Therefore, the integration of the area under those two peaks (64 ppm and 84 ppm) can be an estimation of hemicellulose content in the fiber structure. Figure 6e represents an estimation of the chemical composition of hemp fibers obtained from Solid-state NMR spectra using the Gaussian -Lorentzian model and peak deconvolution.

Thermal stability of hemp fibers. Figures 7a, b, c, d, and e represent the TG and DSC curves of treated and untreated hemp fibers. The heterogeneous chemical composition of natural fibers makes thermal degradation complex. The thermal degradation of hemp fibers from TGA can be divided into three thermal stages including water evaporation at 50°C - 150°C, hemicellulose decomposition at 220°C - 300°C, and cellulose degradation at 300°C - 400°C. However, it is thought that the thermal degradation of lignin begins at roughly 280°C and ends at about 450°C. The complex aromatic nature of lignin enables lignin to keep thermal stability at a higher temperature; therefore, it can slow down the decomposition of cellulose to some extent in terms of the thermal degradation event of cellulose (Viscusi et al. 2021; Fisher
et al. 2002). MWE-DES treated samples and alkali-treated sample both demonstrated a small amount of water evaporation as compared to the raw hemp sample because of the reduction of OH groups. It is evident from the TG thermograms (Figure 7b) that hemicellulose has lower thermal stability as the degradation of hemicellulose observed at 256°C for raw hemp and sample B (on the other side, the absence of the hemicellulose peak in the derivative TG curve indicates the removal of hemicellulose from the samples C, D, and E), which would facilitate the second stage thermal degradation (lignin thermal degradation) for a longer period (Viscusi, Barra, and Gorrasi 2020) which might help lignin to have higher thermal stability. At the third degradation stage, the peak at 300°C - 375°C represents the cellulose degradation, and 375°C - 400°C could be assigned to the oxidative degradation of cellulose. However, DES-treated fibers, especially the samples C, D, and E had higher thermal stability (shifting the degradation peak toward higher temperature in TG curves for all the degummed samples) as the degradation starts from 320°C to 375°C. The main weight loss of raw hemp fibers was recorded at about 225°C - 390°C while the treated hemp fibers showed their main weight loss in the 250°C - 390°C region as can be seen in Figure 7a. The onset points of DES-treated hemp fibers including alkali-treated fibers moved from 287°C to 310°C - 318°C, as similarly found by Fan et al. (Fan 2010) (Table 2). The thermal degradation of cellulosic components usually occurs at higher temperatures compared to that of non-cellulosic components. The increased onset temperatures in MWE-DES treated fibers indicated the removal of non-cellulosic components. The removal of non-cellulosic components helps cellulose to be rearranged in such a way to increase crystallinity with the densely packed rearrangement of glucose molecules, and it renders high thermal stability to cellulose since densely packed crystalline rearrangements slow down thermal decomposition.

Table 2. Summary of TG and DSC data of both raw and degummed hemp fibers (T_D, T_max, and T_g refer to thermal degradation, peak maximum, and glass transition temperatures in the TG and DSC curves)

| Sample ID | TGA | DSC |
|-----------|-----|-----|
|           | Weight Loss (%) | Onset Temp. (°C) | T_max (°C) | T_g (°C) | Enthalpy (J/g) |
|           | 1st T_D | 2nd T_D | 3rd T_D | At 600°C |                  |                  |                  |
| Raw       | 5.246   | 17.21  | 36.65  | 65.28   | 265             | 324             | 250             | 272.09           |
| A         | 3.106   | 9.698  | 55.83  | 77.28   | 311             | 344             | 302             | 111.43           |
| B         | 4.129   | 11.22  | 48.37  | 74.62   | 310             | 340             | 305             | 175.25           |
| C         | 2.842   | 8.500  | 60.23  | 82.22   | 316             | 348             | 400             | 139.13           |
| D         | 2.875   | 7.497  | 60.17  | 78.88   | 322             | 353             | 326             | 215.34           |
| E         | 1.811   | 8.256  | 63.00  | 80.11   | 318             | 349             | 328             | 208.32           |
Bond water (OH groups) to cellulose and hemicellulose have higher thermal stability (Kabir et al. 2013), thus water evaporation occurred in the raw hemp in the range of 50°C - 150°C as seen in the DSC curves (Figure 7e). On the other hand, the range in MWE-DES treated fibers was 50°C - 140°C. Water evaporation for the alkali-treated fibers occurred at 50°C - 135°C (Figure 7a). It can be assumed that there was therefore a reduction of hydroxyl groups in the DES-treated and alkali-treated samples. The removal of hemicellulose and improved hydrophobicity of the treated fibers results in higher thermal stability for cellulosic compounds. According to TG data (Table 2), after 350°C in the first heating run, more than 75% of the hemp samples was decomposed. However, in the DSC Figure 7e, the glass transition of dry cellulose occurs at 200-250°C depending on its molecular weight, crystallinity, and structure (Kubát and Pattyranie 1967). The $T_g$ of 70% crystalline cellulose containing 2% water (playing the role of a plasticizer) drops to 160°C (Szcześniak, Rachocki, and Tritt-Goc 2008). The $T_g$ of the raw hemp sample is clearly observed right around 250°C, but this transition is absent in all other alkali and MWE-DES treated samples, obviously due to the plasticizing effect of some remnants after heating to 150°C (Table 2) since below $T_g$, all materials become rigid, one may conclude that the rigidity of alkali and MWE-DES treated samples is practically absent and these fibers might exhibit a certain degree of elasticity. An exothermic peak was observed at around 370°C for the raw hemp fiber in the DSC curve (Figure 7e). The exothermic peak for the MWE-DES treated fibers was shifted towards a higher temperature and sample D demonstrated an exothermic peak around 450°C, which confirmed the higher thermal stability of the cellulose in the treated fibers. Hemicellulose decomposition occurred between 50°C - 320°C with an exothermic peak at 287°C for raw hemp fibers. The disappearance of this exothermic peak in the treated fibers validated the removal of hemicellulose. MWE-DES treated and alkali-treated fibers showed a small endothermic peak at around 376°C - 390°C (Figure 7e), thus, it can be concluded that the removal of hemicellulose resulted in higher thermal stability of the treated fibers as the broad exothermic peak of cellulose in the raw hemp fibers at about 372°C moved toward 435°C for the alkali-treated fibers, while MWE-DES treated fibers had a peak between 450°C - 473°C. Lignin in natural fibers normally has a decomposition range between 250°C -450°C (Gargol et al. 2021), which is followed by the raw hemp fibers in this study. The aromatic structure of the lignin (aromatic hydrocarbons, hydroxy phenolics, guaiacyl, and syringyl compounds) enables lignin to have a broader range of degradation temperatures, which is supported by the MWE-DES treated fibers and alkalized fibers. However, DES treated fibers and alkalized fibers showed degradation of residual lignin up to 520°C (Figure 7e), indicating higher thermal stability of the treated fibers. In summary, it can be concluded that purification and less variation occurred with MWE-DES treated hemp fibers, which resulted in a higher thermal stability of the treated fibers.

UV shielding performance of hemp fibers. It is evident that all the hemp samples had excellent UV protection properties (all the hemp fiber samples have the transmittance % at a range of 0% - 0.06%) (Figure 8a). Among all the hemp samples, sample C had the lowest UPF value, even though other MWE-DES treated samples also had excellent UPF values (Figure 7b). It is obvious that there is a tendency to have a lower value of UPF after treating with NaOH since aggressive alkali treatment removes most of the lignin content from the fiber surface. The aromatic structure of lignin aids to block the UV radiation in the raw hemp fibers. The phenolic hydroxyl, carboxyl, and carbonyl groups in the lignin structure are
responsible for generating heat when the fiber is subjected to the photon energy of UV light. However, these phenolic groups, especially hydroxyl groups in the lignin could absorb the generated heat and also are able to quench the active radicals through the mechanics of electron transfer (Dean et al. 2013). The presence of lignin in the fiber structure facilitates improved UV blocking performance. For instance, MWE-DES treated fibers at 1:10 fiber-DES ratio (sample B) had a UPF value of about 118 and after NaOH treatment (sample C), the UPF value was reduced to 102.43. A similar trend was observed for samples D and E (Figure 8b).

MWE-DES treatment at 1:20 fiber-DES ratio led to increased UPF values (UPF=183.67) compared with the 1:10 ratio data (UPF=127.47). There are few published studies about the contribution of DES solvent in the degummed lignocellulosic materials in terms of UV protection. However, DES made of glycerol and choline chloride with alpha hydroxylate anions exhibited crosslinking and plasticizing ability in the polysaccharide matrix (Zdanowicz, Jędrzejewski, and Pilawka 2019). The improved UV blocking performance of MWE-DES treated samples could thus be explained by the involvement of DES solvent in the fiber structure. This phenomenon probably happens due to the interference of the DES solvent as a crosslinking and plasticizing agent, forming the DES-fiber complex when it comes to contact with the fiber structure. In addition, the presence of low lignin content in the degummed fibers accelerated the UV shielding performance in the MWE-DES treated fibers.

**Discussion**

MWE-DES treated fibers clearly showed a comparable yield of cellulose with the alkali-treated fibers but within a noticeably short treatment time (60min and 90 min). On the other hand, alkali treatment requires one additional pretreatment process for 1 hr with NaOH. It is plausible that MWE is responsible for exciting the molecular chains of hemp fibers and thereby lignin separation can be facilitated from the lignin-carbohydrate complex. Therefore, the electromagnetic energy of microwave shows a significant role in the yielding of cellulose in the MWE-DES treated fibers. Thermal stability of MWE-DES treated fibers was enhanced as the glass transition \( T_g \) was absent in the MWE-DES treated fibers at 250°C region of the DSC curves and \( T_g \) is dependent on the molecular weight of the cellulosic fibers. Thus, the number of \( \beta-O-4, \beta-\beta, \) and \( \beta-5 \) bonds in the lignin structure was decreased and therefore, the effective lignin fractionization was occurred in the MWE-DES treated fibers.

MWE-DES treated sample at 1:20 fiber-DES ratio has the higher cellulose content with a higher degree of crystallinity as compared to the sample of the treatment at 1:10 ratio. Smink et al. (Smink et al. 2019) found that the addition of choline chloride in the DES made of lactic acid and choline chloride, accelerates the pulping process, meaning that a higher fiber-DES ratio increases the lignin removal. Li et al. (Li et al. 2021) found that choline chloride as a hydrogen bond acceptor with the urea (hydrogen bond donor) is prone to cleave the lignin-carbohydrate linkages than the breakage of hemicellulose linkages. Since the viscosity plays a significant role in the delignification of biomass, the low viscosity of choline chloride and urea-based DES with MWE treatment accelerates the delignification process. A similar result
was found from this work as the rate of lignin removal was higher than the hemicellulose removal. Therefore, DES made of choline chloride and urea is preferred to treat the hemp fibers.

Urea as a hydrogen bond donor in the deep eutectic mixture with choline chloride formed a complex hydrogen bond network between components. It was found that the DES network acts as a three dimensional (3D) structure of complex ions in which involves molecules of two urea, one choline, and one chloride (Hammond, Bowron, and Edler 2016). Therefore, it can be hypothesized that urea helps to stabilize the deep eutectic behavior of the mixture by the formation of complementary hydrogen bond with chloride and choline. Thus, the degumming performance of hemp fibers is dependent on the urea concentration in the DES and especially the molar ratio of urea and choline in the DES. From the NMR analysis of MWE-DES treated fibers, it was confirmed that there was a significant reduction of lignin content in the treated fibers. Therefore, DES made of urea and choline chloride at a 2:1 molar ratio was proven to be an effective deep eutectic mixture in terms of hemp fiber degumming.

Conclusions

Degumming of hemp fibers is crucial for further fiber processing with respect to textile applications or composite manufacturing. A novel method was developed to degum the hemp bast fiber in our study by utilizing DES and MWE. There was no significant difference between MWE-DES treated fibers and traditional alkali-treated fibers in terms of chemical structures, crystallinity, and thermal stability. One step MWE-DES treatment of hemp fibers at 1:10 and 1:20 fiber-DES ratio exhibited effective delignification with clean fiber morphology as lignin content reduced to 6.16% in the treated fibers at 1:20 fiber-DES ratio.

MWE-DES treatment was carried out without the use of water and even combined MWE-DES treatment needs fewer chemical consumptions as compared to the traditional alkali treatment. Therefore, MWE-DES treatment can be a novel path for degumming of natural fibers, including hemp fibers, for the purpose of improving fiber qualities in all distinct aspects of sustainable subsequent fiber processing. Future research can be conducted on the reusability and recovery of used DES liquid.

Declarations

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Author Contributions

All authors contributed to the study conception and design. The study was supervised by Qinglin Wu. Material preparation, data collection and analysis were performed by Bulbul Ahmed. The first draft of the
manuscript was written by Bulbul Ahmed and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Conflicts of Interests**

The authors declare no competing financial interest.

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**Figures**
**Figure 1**

Schematic showing reaction mechanism of DES system made of choline chloride and urea

**Figure 2**

Schematic of hemp fiber degumming process using combined MWE-DES treatment
Figure 3

SEM images of both treated and untreated hemp fibers: (a, b) Raw hemp fibers (Raw); (c, d) alkali-treated fibers (A); (e, f) MWE-DES treated fibers at the solid-liquid ratio of 1:10 (B); (g, h) MWE-DES predegummed at the solid-liquor ratio of 1:10 and alkali-treated fibers (C); (i, j) MWE-DES treated fibers at the solid-liquid ratio of 1:20 (D); (k, l) MWE-DES predegummed at the solid-liquor ratio of 1:20 and alkali-treated fibers (E)
Figure 4

FT-IR spectra of both raw and degummed hemp fiber samples
Figure 5

(a) XRD spectra of raw and degummed hemp fibers and (B, C) crystallite size and crystallinity % of raw and degummed hemp fibers
Figure 6

CP-MAS/13C-NMR spectra (a to d) and chemical component data (e) of raw and degummed hemp fibers
Figure 7

TG (a, b, c, and d) and DSC (e) data of raw and degummed fiber samples

Figure 8

UV-vis spectra (a) and UPF values (b) of both raw and degummed hemp fibers treatment (sample C), the UPF value was reduced to 102.43. A similar trend was observed for samples D and E (Figure 8b).

Supplementary Files

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