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Enhanced mechanical strength and controlled biodegradability of bio-membranes synthesized from waste hemp fibers

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ABSTRACT

In this work, agricultural hemp waste was converted into cationically modified membranes through a two-step procedure. First, the postharvest hemp fibers underwent delignification, after which they were quaternized using a Deep Eutectic Solvent (DES) composed of chlorocholine chloride and urea. The cationized fibers were then pressed and cross-linked with citric acid (CA), a natural cross-linker, to obtain membrane sheets. The untreated fibers (NtHF) and the resulting membranes were characterized by Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Mechanical performance was evaluated by measuring the breaking force and determining the tensile strength using the Brazilian test. Biodegradation was monitored for 90 days in a con-rolled soil-burial environment at 24 °C, comparing membranes made from untreated versus cationized hemp fibers. The modified material exhibited a notable increase in tensile strength (2.41 MPa), attributed to the combined effects of enhanced intermolecular interactions within the cationic hemp matrix and the stronger cross-linking provided by citric acid. Signs of biodegradation appeared after just 14 days, with approximately 25% mass loss. In contrast, the untreated fibers degraded slightly faster, underscoring the stabilizing effect of citric acid.

Keywords: lignocellulose fibers, membranes, Deep eutectic solvent, biodegradability, mechanical properties, Brazilian test.

1. Introduction

The increasing accumulation of agricultural waste represents a significant ecological challenge, necessitating the development of sustainable approaches for its valorization. Industrial hemp (*Cannabis sativa L.),* a widely cultivated plant, generates a substantial amount of lignocellulosic waste fibers after harvest, which typically contain 67.0-78.3% cellulose, 5.5-16.1% hemicellulose, 2.9-3.3% lignin, and 0.8-2.5% pectin (Pejić et al., 2020). These fibers exhibit great potential for transformation into functional materials with improved mechanical and biodegradable properties. Contemporary research in material science emphasizes the importance of modifying natural fibers, such as hemp, flax, jute, or kenaf fibers, to expand their applications, particularly in the production of biodegradable membranes (Shelly et al., 2025). Natural fibers find wide application in various industries, including construction (insulating materials, composites), automotive (interior panels, linings), packaging (biodegradable and compostable packaging), as well as the textile and biomedical industries (bandages, implants, filtration materials). Natural fiber–based composites offer significant potential in contributing to the ultimate goal of automobile manufacturers, which involves achieving a 30% weight reduction and a 20% cost reduction(Biagiotti et al., 2004; Puglia et al., 2005) One of the key strategies for enhancing fiber functionality is chemical modification, such as cationic modification, which can improve the mechanical strength and stability of the material. Deep Eutectic Solvents (DES), a class of environmentally friendly solvents, have proven to be effective reagents for fiber functionalization due to their tunable physicochemical properties and compatibility with natural polymers (Arora et al., 2020). This study presents a two-step chemical treatment of hemp waste fibers using a dimethyl sulfoxide/tetra-n-butylammonium hydroxide (DMSO/TBAOH) system, resulting in regenerated hemp fibers, particularly through the delignification of treated fibers. Quaternary ammonium groups were introduced using a Deep Eutectic Solvent (DES) synthesized from choline chloride and urea as the main components, with chlorocholine chloride prepared following a procedure similar to that reported in (Šebestík et al., 2011). The detailed modification procedure was described in our previous study (Knežević et al., 2024a). As a novel aspect of this work, the functionalized fibers were subsequently incorporated into bio-membranes using citric acid as a natural cross-linker, enabling the formation of a mechanically stable and biodegradable material, as also demonstrated in (Dönitz et al.,

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2023). Structural and chemical characteristics of the synthesized membranes were analyzed using scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy. Additionally, mechanical performance was assessed by measuring tensile strength using the Brazilian test method. The biodegradability of the developed membranes was tested using the Soil burial method (AATCC Test Method 30-1993) over 90 days. Several samples of the same membranes were also made for characterization and biodegradability testing.

When comparing the changes in modified fibers and the membranes produced from them, an unmodified fiber (NtHF) was also fabricated in the form of a membrane, and its characterization is presented in this study. The results show a significant increase in the tensile strength of the membranes made from cationically modified hemp fibers (WCHM), which can be attributed to enhanced intermolecular interactions and more efficient crosslinking with citric acid. This effect is further supported by recent research, as a less-known one-step crosslinking method based on citric acid has been developed in recent years (Salihu et al., 2021). Such an approach reduces the need for pretreatment and has proven effective even for wood impregnation and the processing of agricultural waste (Beluns et al., 2023). For example, Shuaiyang et al. demonstrated xylan crosslinking with citric acid as a potential adsorbent for industrial wastewater treatment (Shuaiyang et al., 2013). Moreover, the biodegradability assessment demonstrated the material's potential for sustainable applications, with a significant mass reduction observed within the first 14 days. The obtained results confirm the sustainability of using hemp waste fibers as a renewable resource for developing high-performance biodegradable membranes, contributing to the advancement of sustainable materials for environmental applications.

2. Experimental sections

2.1. Materials and methods

All chemicals utilized in this research were of analytical grade and used without further purification. The following chemicals were sourced from Sigma Aldrich (Germany): dimethyl sulfoxide (DMSO), urea (U), choline chloride (ChCl), citric acid (CA), and sodium chloride (NaCl). Tetra-n-butylammonium hydroxide (TBAOH) was obtained from Fisher Chemical (UK). Waste hemp fibers were provided by KONOBETON, Novi Sad, Serbia.

The surface structure of NtHF and WCHM was examined using scanning electron microscopy (SEM). Imaging was performed on a Tescan Mira 3 XMU FEG microscope, equipped with a Schottky field emission gun operating at 20 kV (Czech Republic).

The identification of functional groups present in the NtHF and WCHM was carried out using a Nicolet™ iS™10 FT-IR Spectrometer (Thermo Fisher Scientific, USA), equipped with Smart iTR™ Attenuated Total Reflectance (ATR). Spectra were recorded within the wavenumber range of 4000–500 cm^{-1}.

Testing the mechanical properties is a crucial part of material characterization for industrial applications, for example, in the shipbuilding industry. The importance of the strength and fire resistance of hemp fibres has been highlighted in recent studies conducted by Scheibe, M. (Scheibe et al., 2025). In this work, the mechanical properties of both membranes were assessed using an Instron 1332 testing machine equipped with 100 kN and 5 kN load cells connected to the acquisition system (Navidtehrani et al., 2022). Tensile strength measurements were performed by applying force until the samples fractured. The breaking force was recorded, and tensile strength was calculated according to the Brazilian test method (Fairhurst, 1964). The equation used for the Brazilian test is provided in the Supplementary Material (Knežević et al., 2024a).

The biodegradability of the membranes was evaluated through the Soil Burial Test (AATCC Test Method 30-1993). Samples were incubated in a controlled laboratory (Knežević et al., 2024) setting at a constant temperature of 24 °C for 90 days. The equation for calculating lost mass is presented in our paper (Knežević et al., 2023).

2.1.1. Preparation of WCHM

Following the washing of waste hemp fibers with distilled water, chemical modification was conducted using the DMSO/TBAOH system to achieve defibrillation of fibers (Sirviö et al., 2021). This was followed by treatment with a synthesized Deep eutectic solvent (DES) composed of chlorocholine chloride and urea (DES-HF) (Šebestík et al., 2011). Finally, membrane fabrication was carried out through cross-linking with citric acid, as outlined in our previous research (Knežević et al., 2023)

3. Results and discussion

3.1. SEM analysis

The SEM analysis revealed the surface morphology of NtHF and WCHM, as depicted in Figure 1.

Figure 1a presents the fiber surface, which has been smoothed and cleaned to achieve a more active surface for the subsequent functionalization process and cross-linking through the addition of citric acid. Raw hemp fibers (Figure 1a) contain lignin, hemicellulose, oils, waxes, and pectin, resulting in a rough and rigid fiber surface, as observed in the SEM images. SEM analysis of the membrane (Figure 1b) confirms its successful synthesis, revealing a well-defined network of

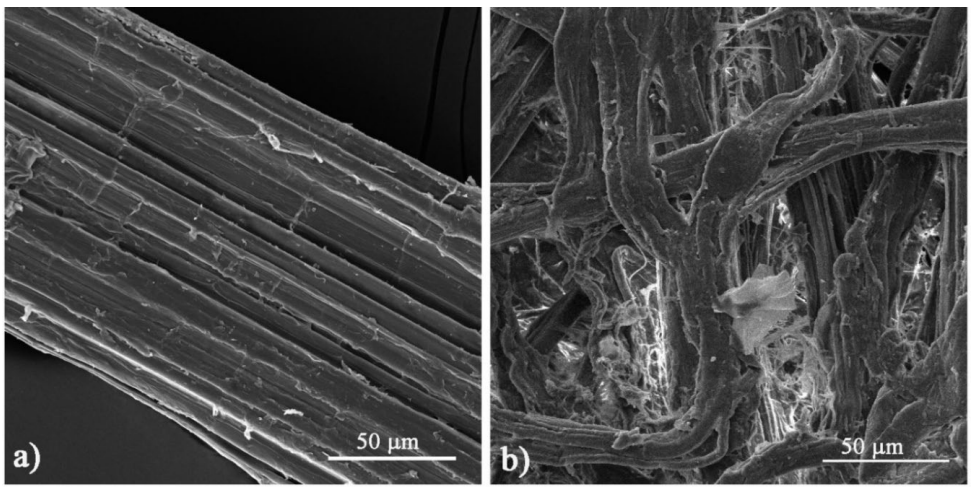


Fig. 1. SEM micrographs of (a) NtHM, and (b) WCHM (Knežević et al., 2024)

densely packed fibers with a relatively uniform surface. This uniformity can be attributed to the effect of citric acid and the subsequent pressing process, which shapes the material into a membrane structure. The image on the right exhibits a larger surface area compared to the left image, despite being captured at the same magnification.

3.2. FTIR analysis

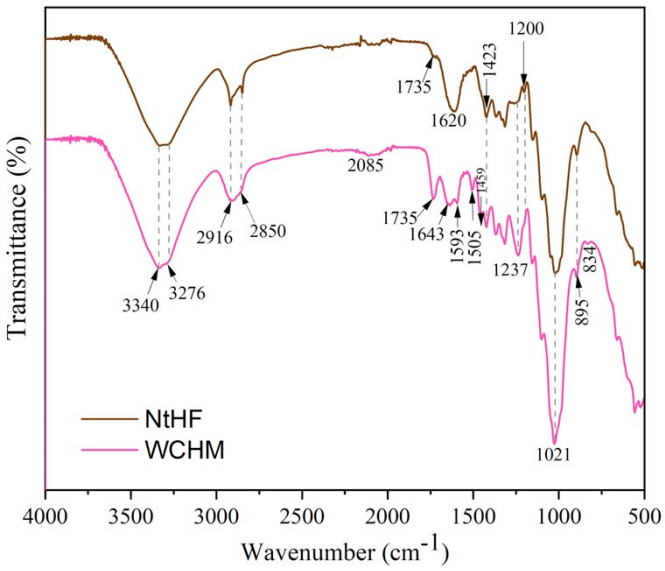


Fig. 2. FTIR spectrum of nontreated fibers and modified membrane

The FTIR spectra of NtHF and WCHM samples exhibit a broad band with two peaks at 3340 and 3276 cm-^{1}, which are attributed to the stretching vibrations of the O-H hydroxyl bond in cellulose and lignin (Viscusi et al., 2020) . The peaks at 2916 cm^{-1} and 2850 cm^{-1} originate from the symmetric and asymmetric stretching vibrations of C-H bonds in the methyl and methylene groups of the lignocellulosic structure of hemp fibers (Arora et al., 2020; Matykiewicz et al., 2021). In the spectrum of NtHF, the stretching vibration of ester (C=O) groups from acetyl and carboxyl groups in hemicellulose and lignin is detected at 1735 cm^{-1}. The same peak appears in the WCHM spectrum but with significantly higher intensity and width, indicating crosslinking with CA and the formation of ester C=O bonds (Viscusi et al., 2020). The intensity of the broad band at 1620 cm^{-1} corresponds to the bending vibrations of O-H bonds from absorbed water in cellulose. Symmetric and asymmetric vibrations of C-O-C, C-O, and C-OH from phenolic groups, as well as pyranose ring structures in cellulose, hemicellulose, and lignin, are observed in the range of 1237-1021 cm^{-1}. The band at 895 cm^{-1} is attributed to $\beta(1\rightarrow4)$ glycosidic bonds in cellulose polysaccharides (Kalisz et al., 2021). Upon reaction of the modification agents with hemp fibers, new peaks at 2085, 1593, 1505, and 1459 cm^{-1} appear, which are assigned to the quaternary ammonium cation (≡N^{+}–), asymmetric and symmetric bending vibrations of NH_3^+, C-H bending in CH_3 and CH_2 groups attached to ≡N^{+}–, and N-H rocking vibrations, respectively (Yang et al., 2019). The O-H bending vibration in cellulose shifts to a higher wavenumber (1643 cm^{-1}) after modification, indicating intermolecular hydrogen bonding interactions between the lone electron pair of oxygen in O-H groups of cellulose and the quaternary ≡N^{+}– group. Compared to the reference sample NtHF, the WCHM spectrum exhibits an increased intensity of bands in the range of 1423-895 cm^{-1}, suggesting that carbon-ether and aryl-ether linkages between polysaccharides and the lignin structure remain intact during modification.

3.3. Mechanical properties of the membrane

The results of the Brazilian test (Figure 3) show that the membrane prepared from untreated fibers exhibits a tensile strength (σ) of only 0.35 MPa (Knežević et al., 2024). Figure 3 illustrates the laboratory setup of the Brazilian test, with the left panel showing the complete testing assembly and the right panel providing a close-up of the circular membrane specimen positioned between the loading plates. Functionalization of the fiber surface with a quaternary group slightly improves the intermolecular interactions between cellulose chains. Furthermore, the combined effect of weaker physical interactions among ChClU fibers and stronger covalent cross-linking with citric acid leads to a markedly enhanced tensile strength of 2.41 MPa.

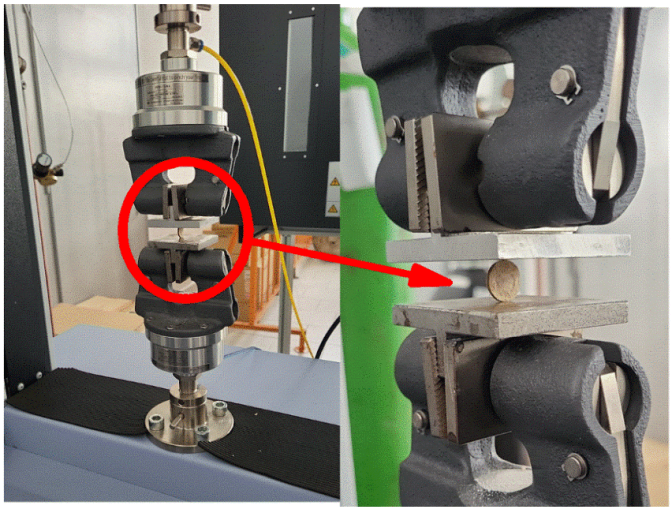


Fig. 3. Demonstration of the Brazilian test on the synthesized membrane

3.4. Biodegradability of the membrane

Evaluating the mass loss of hemp fibers following burial in soil is part of the biodegradation assessment process for both untreated and modified hemp fibers. As seen in Figure 4, the mass loss is represented as a percentage in relation to the original samples. The findings for untreated fibers are consistent with predictions, showing that mass loss rises with extended exposure to soil microbes. The higher moisture absorption and retention capacity of cross-linked modified fibers causes an accelerated biodegradation rate, which is why nontreated fibers degrade more quickly (36.16% after 14 days and 99.1% after 49 days) than cross-linked modified fibers (25.31% after 14 days) (Brunšek et al., 2023). Furthermore, ammonium groups, which are recognized for their antibacterial qualities (Wen et al., 2015) slow down the initial degradation process by preventing bacterial development in its early phases. Additionally, unlike WCHM, which has reduced porosity and a more linked cellulose polymer structure, increasing resistance to enzymatic hydrolysis, the material's fractures and porosity promote microbial colonization and accelerate breakdown rates. Between the 7th and the 35th day of the biodegradation trials, there is a transitional phase of structural disintegration. The nontreated membrane showed a consistent disintegration rate of 99.1% after 49 and 60 days, according to the biodegradation tests, while WCHM degraded to 49.7% after 42 days. The untreated membrane was completely biodegraded by day 49, although WCHM degradation persisted after 60 days. However, both membranes showed morphological alterations, with fibers progressively separating. The influence and biodegradation potential of hemp fibers were also demonstrated in the study by Lim and Jung (2025) (Lim et al., 2025), in which torrefaction of hemp fibers was performed and the biodegradability of the PHA/HF-200 composite was investigated. The results showed that complete biodegradation of the composite was achieved after 40 days, confirming its environmental sustainability.

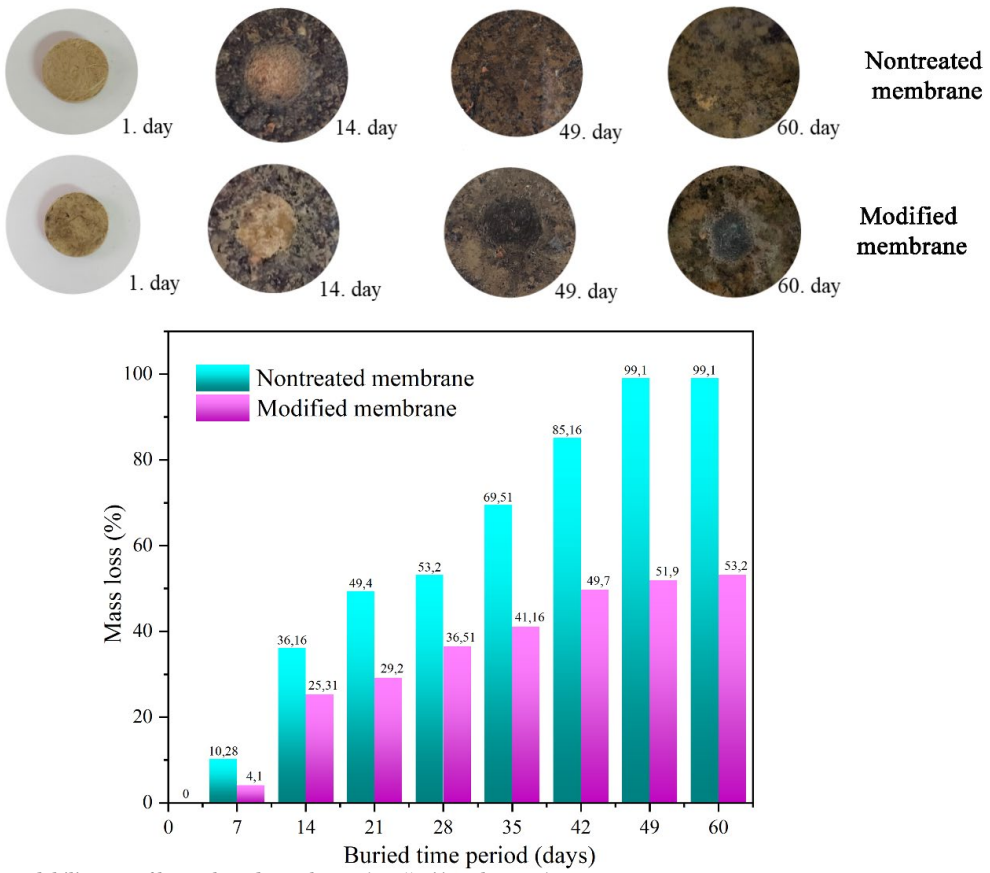


Fig. 4. Results of the biodegradability test of hemp-based membrane (Knežević et al., 2024)

Conclusion

Through a two-step chemical modification and citric acid cross-linking technique, the current work successfully demonstrates the value-adding of agricultural hemp waste into mechanically durable and biodegradable membranes. In comparison to untreated hemp fiber membranes (NtHF), the addition of quaternary ammonium groups greatly strengthened intermolecular connections and increased tensile strength by about seven times. Both untreated and cationically modified hemp membranes (WCHM) are biodegradable, according to soil burial experiments; cationic functionalization and citric acid cross-linking slow down the pace of disintegration and increase the material's lifespan (up to 60 days). According to the findings, leftover hemp fibers provide an inexpensive and renewable source of raw materials for creating bio-membranes with specific mechanical (tensile strength of 2.41 MPa) and degrading characteristics. Future research might concentrate on expanding the manufacturing process, incorporating additional natural polymers or fillers to further adjust mechanical and degradation characteristics, and investigating specific uses like controlled-release agricultural materials, water purification membranes, or sustainable packaging. With increasing commercial interest in hemp-derived biomaterials for sustainable product development, hemp-based membranes are positioned as a possible substitute for synthetic polymers due to their proven performance and biodegradability.

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Data Availability Statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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