

Utilization of Pineapple leaf – Derived Cellulose Membranes for Separation of Oil in Water Emulsions

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In this study, cellulose membranes were successfully synthesized from pineapple leaves – an abundant agricultural by-product in Vietnam. The membranes were characterized for their structural, morphological, surface, and thermal properties using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET) surface area analysis. The effect of treatment temperature on the alteration of cellulose membrane properties was also investigated. Results from FTIR, SEM and BET indicated that membranes treated at 70 °C exhibited increased hydrogen bonds between cellulose chains and form pores due to the overlapping of cellulose fibers. As a result, the membrane maintained and enhanced the hydrophilic and oleophobic properties of cellulose materials. The efficiency of cellulose membranes in separating oil-water emulsions was evaluated according to SMEWW 5520B:2017. The results showed that after five consecutive separation cycles, the efficiency of the membranes treated at temperatures from 40 °C to 70 °C was above 90%, and the efficiency increased gradually with temperature, from 94.3 % to 99.9% in the 70 °C sample. These results demonstrate the feasibility of utilizing pineapple leaves to prepare cellulose membranes for oil in water emulsion separation applications.

1. Introduction

The rapid growth of modern industries has resulted in the discharge of oily wastewater from oil exploitation, refining, and mechanical processing, leading to increasingly severe water pollution problems. Toxic substances in oily wastewater pose serious risks not only to human health but also to aquatic ecosystems, while oil spills represent a long-term threat to the environment (Putatunda et al., 2019). In addition, the presence of oil in wastewater represents a loss of valuable resources. Therefore, the separation of oily substances from wastewater prior to discharge is of great urgency. Among the various forms of oily wastewater, oil-in-water emulsions are particularly difficult to remove due to their small droplet size (<20 μm), strong interfacial stability, and high resistance to separation.

Oi-in-water emulsion separation can be achieved by physical, chemical, and biological methods. Chemical methods such as coagulation (Bejczy et al., 2024; Chaprão et al., 2018), electrochemical processes (Ajao et al., 2018), carbon-based adsorbents (Wai et al., 2019) have been widely applied. These studies report oil removal efficiencies of about 91–92% for coagulation, and up to 99% when using electrochemical treatment or carbon-based nanomaterials such as magnetic graphene oxide, reduced graphene oxide (rGO), and polyvinyl alcohol-grafted carbon black, with treatment times of less than 30 minutes (Wang et al., 2018; Liu et al., 2017). However, the major drawbacks of these methods include the generation of large amounts of sludge requiring secondary treatment (Hui et al., 2020), high operating costs, electrode corrosion, and the need for pH control (Bleeke et al., 2015). Membrane filtration can also achieve high efficiencies, but suffers from poor long-term stability, fouling, and short membrane lifetime (Shi et al., 2014). For instance, polymer membranes are widely used in oil refining, yet fouling leads to reduced flux and declining separation performance during operation. Although regeneration can be attempted through chemical cleaning with strong oxidants (Cao et al., 2016) or photocatalysis (Kimura et al., 2016), these methods cause membrane degradation, reduced wettability, shortened lifespan, and secondary by products requiring further treatment.

To address these limitations, recent studies have focused on developing renewable natural materials such as cellulose aerogel (Vo et al., 2022), cellulose composite (Tran et al., 2022) and cellulose membranes (Chel-Ken Chiam et al, 2024) for oil in water emulsion treatment. Cellulose possesses a natural fibrous structure and high hydrophilicity, making it particularly attractive for anti-fouling and consistent filtration performance. In this study, pineapple leaves — an abundant agricultural by product in Vietnam rich in cellulose were utilized as a raw material for biofilter membrane fabrication. Cellulose membranes derived from pineapple leaf fibers are not only biodegradable and environmentally friendly but also exhibit a unique natural fiber structure with high hydrophilicity, demonstrating strong potential for oil-in-water separation. The novelty of this work lies in the utilization of pineapple leaf-derived cellulose membranes for oil-in-water emulsion separation, combined with an optimization of the fiber processing route to achieve stable separation performance. To the best of our knowledge, this is the first systematic study investigating cellulose membranes derived from pineapple leaf fibers for oil-in-water emulsion treatment. This approach offers a sustainable, eco-friendly, and cost-effective solution for oily wastewater treatment.

2. Experiment

2.1 Materials

The chemicals used in this study included sodium hydroxide (NaOH, 99.5% purity) and acetic acid (CH₃COOH, 99%) obtained from China, while sodium chlorite (NaClO₂, 80–83% purity) and Tween 80 were purchased from India. Regarding raw materials, pineapple leaves were collected from Tay Ninh Province, Vietnam, and crude oil was obtained from the Bach Ho oil field.

2.2 Preparation of cellulose membrane

The preparation of cellulose membrane from pineapple leaves was carried out according to the following procedure: The collected pineapple leaves were washed with water and ethanol, then dried at 70–75 °C for 48–72 h and finely ground into powder. This powder was further cleaned by repeated washing with water and acetone. Subsequently, it was soaked in an 800 mL 5 % (w/v) NaOH of solution and stirred vigorously at 75 °C for 24 h to breakdown the cellulose structure and partly remove hemicellulose and lignin. The mixture was then washed with deionized water (DI) until pH 7. The cellulose was further treated with 400 mL of a mixed solution containing NaClO₂ 2 % and 3 mL of acetic acid and stirred continuously at 70 °C for 3 h to promote bonding between cellulose fibers. The product was washed several times with DI water, adjusted to pH 7, and finally cast into a cellulose membrane using a non-stick Teflon pan.

2.3 Characterization of the membrane

Fourier-transform infrared spectroscopy (FTIR) was used to analyze the characteristic peaks of the cellulose membrane prepared at four different temperatures (40, 50, 60, and 70 °C) and untreated leaf powder. The samples were evaluated using an FTIR spectrometer (EQUINOX 55, Bruker, Germany). The powdered material was mixed with KBr and recorded in the wavenumber range of 400 - 4000 cm⁻¹.

Scanning electron microscopy (SEM, Hitachi, Japan) was employed to examine the surface morphology of the untreated leaf powder and cellulose membranes prepared at different temperatures (40 - 70 °C). Each sample was scanned at accelerating voltages ranging from 5 to 20 kV.

Thermogravimetric analysis (TGA) was conducted to evaluate the weight loss of the samples with increasing temperature. The analysis was carried out from ambient temperature to 600 °C under a nitrogen atmosphere at a flow rate of 40 mL/min, with a heating rate of 15 °C/min.

Surface area determination of the material was carried out using a TriStar II Plus 3030 analysers.

2.4 Oil – water emulsion separation experiment

The emulsion separation procedure was carried out by filtering 500 mL of emulsion sequentially through the cellulose membrane in five successive cycles. The final filtrate was analysed for residual oil content using liquid–liquid extraction and weight partitioning (SMEWW 5520B:2017). The separation efficiency was calculated according to the following equation:

$$H_e = \frac{C_o - C_i}{C_o} \times 100 \quad (1)$$

where C_o and C_i represent the oil content in the initial emulsion and in the filtrate, respectively.

The crude oil emulsion used for testing was prepared with a mass ratio of 10 % (50 g of crude oil from the Bach Ho oil field, 450 mL of distilled water, and 0.005 g of Tween 80), followed by stirring at 1000 rpm for 20 min. The separation efficiency of the cellulose membranes was examined at different drying temperatures: 40, 50, 60, and 70 °C.

3. Results and discussion

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3.1 Structural and Physicochemical properties of cellulose membranes

The thermal stability of the cellulose membranes was evaluated by thermogravimetric analysis (TGA), with the results are presented in Figure 1 a. In the temperature range of 25 - 150 °C, a slight mass loss of 5 - 10% was observed, primarily attributed to the evaporation of adsorbed water. This water loss was most pronounced in the untreated raw sample compared with the heat-treated ones. The most significant weight loss occurred between 200 and 350 °C, corresponding to the thermal decomposition of hemicellulose and cellulose, resulting in a total mass loss of 60 - 70%. At higher temperatures (400–600 °C), the degradation rate slowed down considerably, accounting for an additional ~20%. This stage is likely associated with the decomposition of residual lignin or the carbonization of the samples.

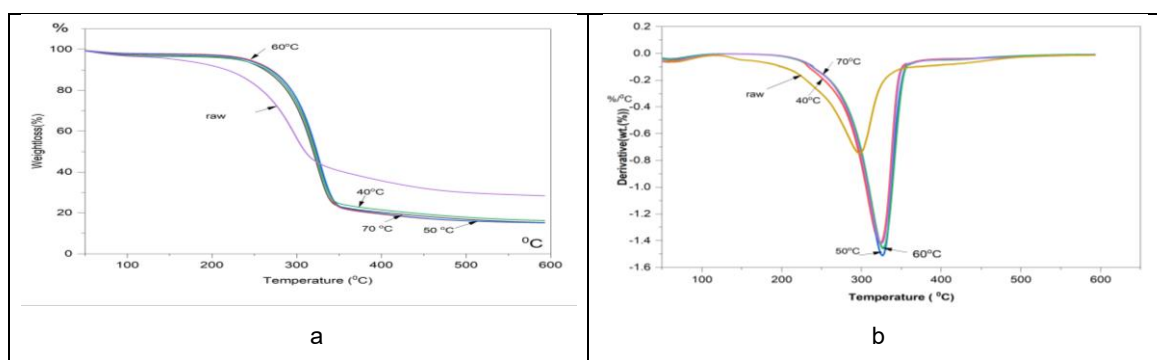


Figure 1: a) TGA curve showing weight loss as a function of temperature, b) Derivative thermogravimetric (DTG) curve of the sample

The DTG curves (Figure 1b) exhibit a peak at approximately 300 - 320 °C, corresponding to the thermal degradation of cellulose and hemicellulose. The untreated raw sample exhibited a broad peak, whereas the four heat-treated samples showed sharper peaks. In particular, the sample dried at 70 °C exhibited a rightward shift with greater intensity, suggesting a more thermally stable structure and higher purity.

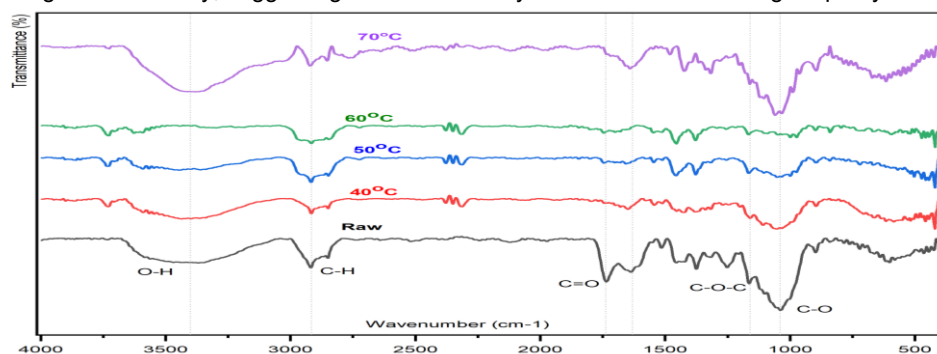


Figure 2: FTIR spectra of cellulose membranes prepared from pineapple leaves

Figure 2 presents the Fourier transform infrared (FTIR) spectra of cellulose samples dried at different temperatures (40, 50, 60, 70 °C) and of the untreated raw sample. A broad absorption band at 3300 - 3400 cm^{-1} , assigned to the stretching vibration of hydroxyl groups ($-\text{OH}$), reflects intra- and intermolecular hydrogen bonds in the cellulose structure as well as the presence of adsorbed water molecules (Zhangdi et al., 2021). The intensity of this band gradually decreased in the sample heat-treated at 70 °C, indicating the progressive loss of adsorbed water and significant alterations in the hydrogen-bonding network. The band around 2900 cm^{-1} , corresponding to C-H stretching vibrations in the polysaccharide chain, remained nearly unchanged across all samples. In contrast, the distinct absorption band at 1730 cm^{-1} , attributed to the C=O stretching vibration of hemicellulose, was clearly observed in the untreated sample but markedly decreased after heat treatment. This observation suggests that mild thermal treatment contributed to the reduction of polar functional groups on the membrane surface. In addition, characteristic cellulose absorption bands were present in all

samples: the band at 1160 cm^{-1} corresponds to the asymmetric C–O–C stretching vibration of the glycosidic bond, whereas the strong band at $1050\text{--}1030\text{ cm}^{-1}$ is attributed to C–O stretching vibrations of C–OH and C–O–C groups in the pyranose ring. These results indicate that the fundamental cellulose backbone remained intact despite heat treatment. Overall, FTIR analysis confirmed that heat treatment enhanced hydrogen bonding between cellulose chains while preserving the cellulose backbone. Meanwhile, the removal of hemicellulose reduced the polar groups responsible for water absorption, thereby minimizing membrane swelling and improving both stability and selectivity. To further corroborate these structural insights, SEM imaging was employed to visualize the morphological evolution of cellulose fibers.

The surface morphology of cellulose was examined by scanning electron microscopy (SEM) at $\times 250$ magnification (Figure 3). The raw samples appeared as compacted sheets with relatively flat surfaces and no fibril separation was observed. In contrast, the heat-treated samples ($40\text{--}70\text{ }^{\circ}\text{C}$) showed a gradual disintegration of the fibril bundles, with thinner fibrils protruding from the main structure. This suggests that the heat treatment disrupted the interfacial interactions and removed non-cellulose impurities. At $50\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$, cellulose exhibited a dense interwoven fibril network consisting of both large and fine fibrils. Notably, the $70\text{ }^{\circ}\text{C}$ dried sample clearly exhibited a heterogeneous network in which large diameter cellulose fibrils intermingled with fine fibrils, forming an overlapping hydrogen-bonded structure with irregular pores. The presence of these pores contributed to the formation of a porous membrane structure, enhancing water permeability.

SEM observations confirmed the gradual disintegration of cellulose bundles from the initial sheet-like configuration into smaller fibrillar networks. This morphological transformation demonstrates the effectiveness of the thermal treatment.

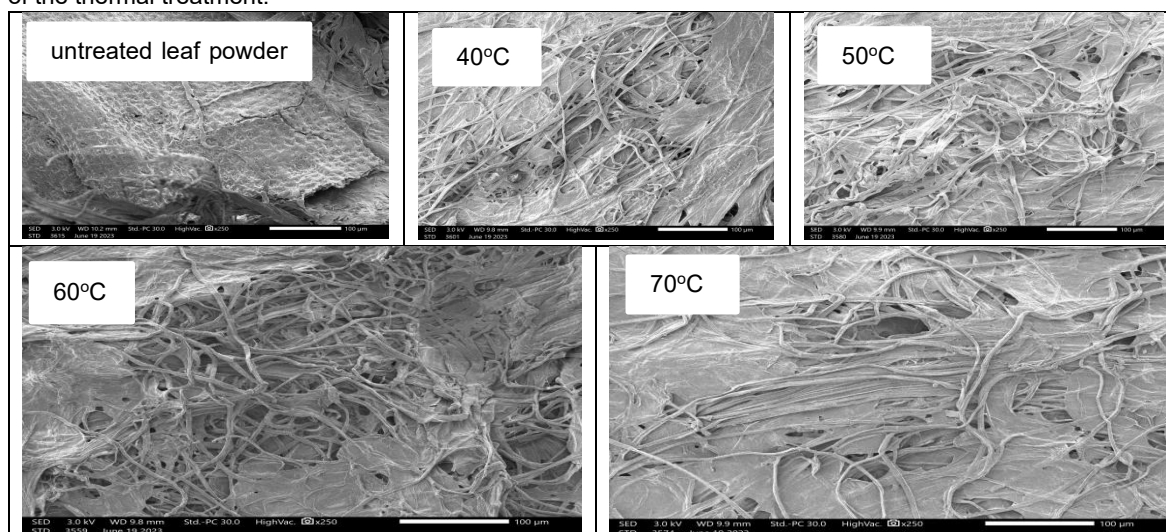


Figure 3: SEM images of untreated leaf powder and cellulose membranes heat-treated at different temperatures (40, 50, 60, and $70\text{ }^{\circ}\text{C}$)

Following the morphological analysis by SEM, the surface textural properties of the cellulose membranes were further examined using nitrogen adsorption - desorption isotherms and the (BET) model. The adsorption - desorption isotherm (Figure 4a) shows that the desorption branch lies above the adsorption branch, forming a hysteresis loop (H3 type). The relatively narrow width of the hysteresis loop suggests that the pore shape is not highly asymmetric. The loop becomes evident in the P/P_0 range of $0.2 - 0.8$ and broadens at higher relative pressures, reflecting the presence of irregular pores formed between cellulose fibers. At low relative pressure ($P/P_0 < 0.1$), the adsorption volume remains very low ($0.05 - 0.15\text{ cm}^3/\text{g STP}$), indicating the absence of micropores, which is consistent with the native cellulose structure. At $P/P_0 > 0.8$, the sharp increase in adsorption reflects the development of large, interconnected voids between fiber bundles. These features suggest that the synthesized cellulose membrane exhibits a slit-like capillary structure which, combined with the inherent hydrophilicity of cellulose, facilitates water permeation while retaining larger oil droplets. Based on the parameters derived from the BET linear plot (Figure 4b), the specific surface area of the cellulose membrane from pineapple leaf fibers was calculated. The specific surface area is relatively low ($0.52\text{ m}^2/\text{g}$), indicating limited porosity. This finding is consistent with the natural cellulose structure, where extensive hydrogen bonding between fibers forms compact bundles with few internal voids. Such structural compactness endows the synthesized material with high mechanical strength, reduced swelling in aqueous environments, and reliable selectivity when applied to oil - water emulsion separation.

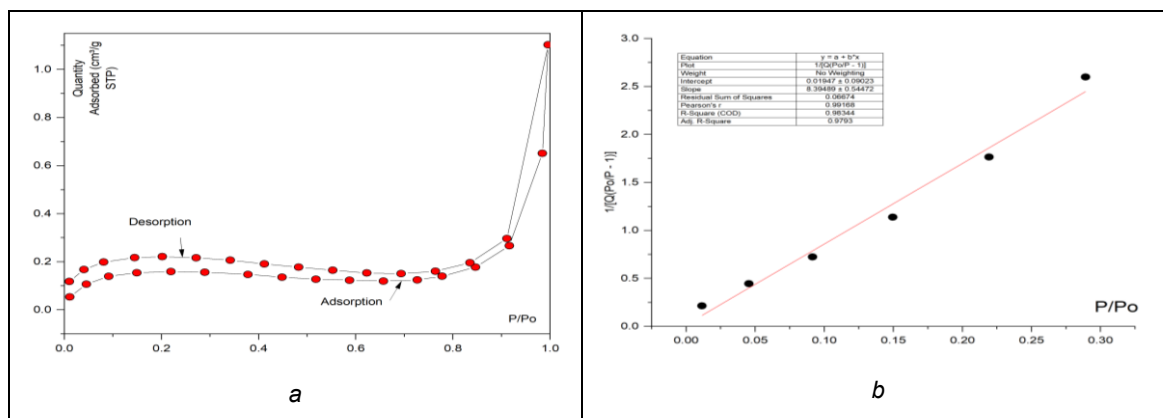


Figure 4: a) N_2 adsorption–desorption isotherm of cellulose membrane heat-treated at 70 °C, b) Linear regression plot of the BET equation

3.2 Emulsion separation performance of cellulose membranes

Figure 5 (a, b) presents cellulose membranes treated at 70 °C and their application in the separation of emulsion samples. Experimental results indicated that increasing the treatment temperature from 40 °C to 70 °C enhanced the oil–water emulsion separation efficiency from 94.3 % to 99.9 % (Figure 5 c).

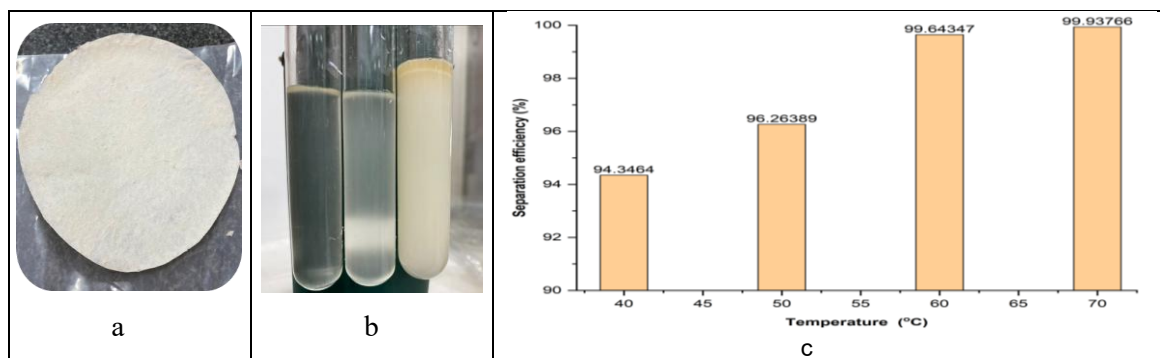


Figure 5: a) Photographs of cellulose membranes dried at 70 °C, b) Emulsion samples before and after treatment, c) Effect of treatment temperature on the emulsion separation performance of cellulose membranes

This enhancement can be attributed to the substantial increase in overlapping hydrogen bonds among cellulose fibers, which promoted the formation of additional pores within the membrane structure (Laivins, 2024). The oil separation mechanism relies on the hydrophilic - oleophobic properties and the capillary sieving effect of cellulose membranes (Zhang et al., 2013; Zhu et al., 2014). Water readily permeates the capillaries through hydrogen bonding with –OH groups, whereas oil droplets are impeded by the oleophobic surface and the water layer covering the capillaries. Drying at 80 °C caused membrane shrinkage and yellowing, likely from rapid water evaporation, capillary collapse, and partial lignin oxidation (Koo, 2020). Therefore, the optimal drying temperature is 60 - 70 °C. In comparison with previously reported natural cellulose materials such as rice husk (Shen et al., 2024) and wood (Hu et al., 2019), applied to crude oil–water and edible oil–water emulsions, the separation efficiencies ranged from 94.8 - 99.1 % and > 98 - 99 %, respectively. These findings demonstrate the feasibility of cellulose membranes derived from pineapple leaves and highlight their potential for sustainable and eco-friendly oil–water wastewater treatment.

4. Conclusion

Cellulose membranes were successfully synthesized from pineapple leaf powder through alkali treatment, bleaching, and membrane formation. Physicochemical analyses (TGA, FTIR, BET, SEM) confirmed a structure composed of fine cellulose fibers with interconnected pores, providing mechanical stability and enabling selective water permeation. The membranes achieved oil in water emulsion separation efficiencies above 90%, with optimal performance at 70 °C. However, drying at temperatures above 80 °C triggered structural shrinkage and reduced efficiency, highlighting the necessity of controlled thermal processing. These findings underscore the potential of pineapple leaf - derived cellulose membranes as sustainable and eco - friendly oil - water

separation applications. Future studies will focus on enhancing reusability, durability, throughput, as well as incorporating additional functionalities such as antibacterial activity and improved separation for diverse emulsion types.

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