Supplementary Information (SI) for RSC Sustainability.

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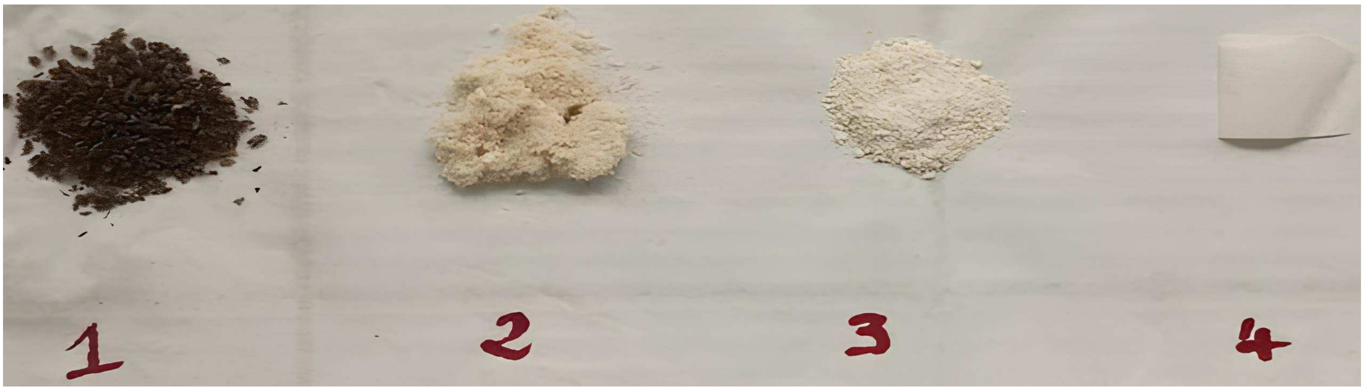
Plus qu'une formation, un avenir à construire

Nanofiltration membranes based on cellulose triacetate from millet husk

Preparation process



Dr. Maryam Khadim MBACKE

Amadou Mahtar Mbow University Diamniadio/Senegal

Introduction

Millet (Pennisetum glaucum) is the dominant cereal crop in Senegal in terms of cultivated area and represents a staple food for both urban and rural populations. Beyond human consumption, millet is extensively used for livestock and poultry feeding. National production was estimated at approximately 0.9–1.0 million tonnes in the 2020/2021 season, generating about 1.13 million tonnes of agricultural residues annually. The economic value of millet production in Senegal is conservatively estimated to exceed USD 1 billion per year. Despite this substantial production capacity, existing research has largely focused on agronomic productivity, whereas the downstream valorisation of by-products—an important driver of local value creation and employment, particularly for women—remains underexplored.

Primary processing of millet produces large quantities of husk, a cellulose-rich lignocellulosic residue. Current valorization pathways are mainly limited to low-value applications such as construction materials, biochar production, composting and animal feed. Developing higher-value conversion routes for this biomass therefore represents a strategic opportunity to enhance circularity and local manufacturing value.

In this context, the present work explores an alternative valorization strategy based on the extraction of cellulose from millet husk and its conversion into cellulose triacetate (CTA), followed by the fabrication of nanofiltration membranes. Cellulose extraction and CTA synthesis were carried out at the Chemistry Laboratory of Amadou Mahtar Mbow University (UAM), while membrane preparation and advanced characterization were performed at the Institute of Chemical Sciences of Rennes (UMR CNRS 6226), within the Chemistry and Process Engineering Team, under the supervision of Prof. Anthony Szymczyk. This collaborative approach enabled the integration of locally sourced biomass valorization with state-of-the-art membrane engineering, contributing to the development of sustainable, bio-based separation materials.

A/Preparation of cellulose acetate polymer solutions and solvent selection

The preparation of cellulose triacetate (CTA) casting solutions was designed to ensure full polymer dissolution, stable rheological behavior, and compatibility with the optimized membrane fabrication conditions targeting balanced permeability, selectivity, and structural stability.

The choice of solvent was guided by Hansen solubility parameter theory to ensure adequate thermodynamic compatibility between the solvent and the synthesized cellulose acetate, whose exact degree of substitution (DS) had not yet been fully confirmed at this stage.

Cellulose acetate with a DS between 2.0 and 2.5 (cellulose diacetate) is known to exhibit good solubility in polar aprotic solvents such as acetone and methyl acetate, whereas cellulose triacetate

(DS ≈ 3.0) preferentially dissolves in chlorinated solvents including dichloromethane and chloroform.

Accordingly, acetone, DCM, and chloroform were systematically evaluated in combination with plasticizers to identify formulations capable of producing homogeneous, viscous, and defect-free casting dopes suitable for phase inversion.

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Protocol 1

Cellulose acetate (5.0 g) was dispersed in acetone (50.0 g) under magnetic stirring for 1 h. Calcium carbonate (10.25 g) and glycerol (4.40 g) were subsequently added and stirring was continued until apparent homogenization. Glycerol was used as a plasticizer, while calcium carbonate was introduced as a dispersing agent. The resulting mixture remained heterogeneous and exhibited incomplete polymer dissolution. Ultrasonic treatment (15 min) was therefore applied to enhance dispersion; however, full homogenization was not achieved.

Protocol 2

Cellulose acetate (5.0 g) was mixed with chloroform (30.0 g) and polyethylene glycol (PEG 600, 3.50 g) and stirred for 3 h, followed by a resting period of 1 h to allow stabilization. The obtained solution remained heterogeneous and exhibited low viscosity, making it unsuitable for membrane casting.

Protocol 3

Cellulose acetate (5.0 g) was dissolved in solvent (51.25 g) in the presence of plasticizer (6.25 g) under continuous stirring for 24 h, followed by equilibration for 1 h prior to use. In this protocol, the three solvents (acetone, chloroform, and dichloromethane) and two plasticizers (glycerol and PEG 600) were systematically evaluated.

Preliminary screening experiments demonstrated that acetone-based formulations led to incomplete polymer dissolution and poor solution homogeneity, even after ultrasonic treatment. DCM -based systems yielded low-viscosity solutions with insufficient stability for reproducible membrane casting. In contrast, Chloroform -based formulations exhibited rapid and complete CTA dissolution, stable viscosity, and excellent optical homogeneity, indicating favorable thermodynamic compatibility with the synthesized polymer.

Plasticizer screening was conducted using glycerol and polyethylene glycol (PEG 600).

B/Preparation of membranes

Polymer solutions prepared with the three protocols were spread using an Elcometer 4340 Automatic Film Applicator.

Fig. 1: Stages of film preparation

The films are left under vacuum to allow the solvent to evaporate.

The films are then immersed in a water bath for the immersion precipitation phase.

Fig. 2: Precipitation phase by immersion in water

The membranes are then placed on absorbent paper to dry.

The membranes from protocol 1 were not recovered because they were dispersed in the acid bath.

The membranes from protocol 2 presented the following appearance:

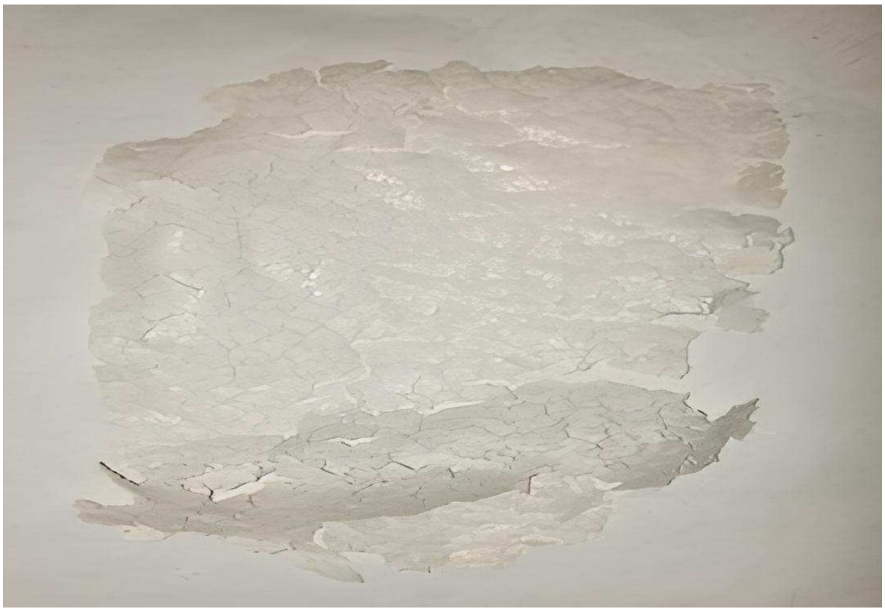

Fig. 3: Membrane from protocol 2

The different solvents and thickeners in the case of protocol 3 gave the following membranes.

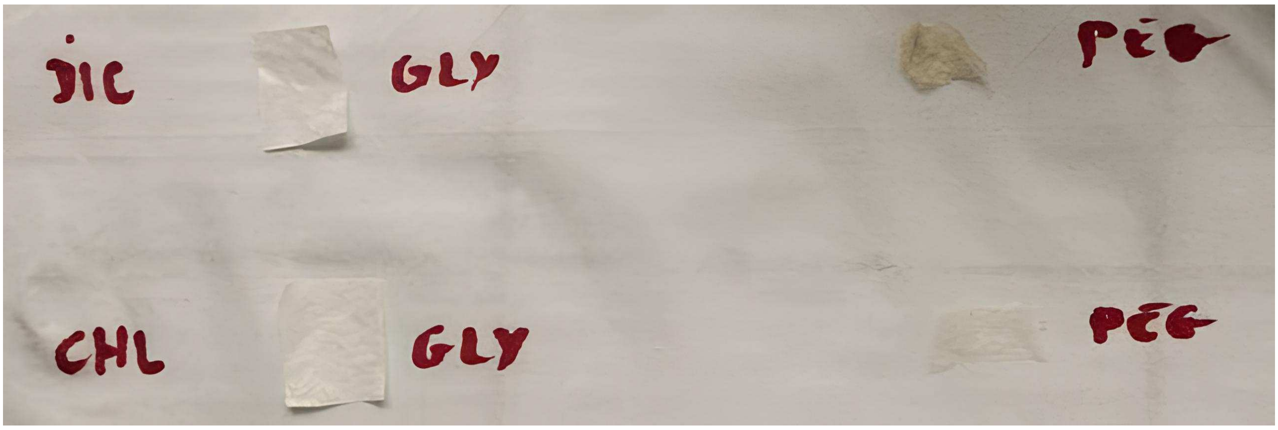

Fig.4: Appearance of the membrane depending on the type of plasticizer

Films prepared in the presence of acetone and PEG600 could not be recovered during the precipitation phase.

Glycerol was selected as the preferred additive due to its ability to enhance hydrophilicity, promote controlled pore formation, and improve mechanical flexibility without inducing excessive macrovoid development. PEG-containing solutions showed lower viscosity and reduced stability, which limited their applicability for controlled membrane formation.

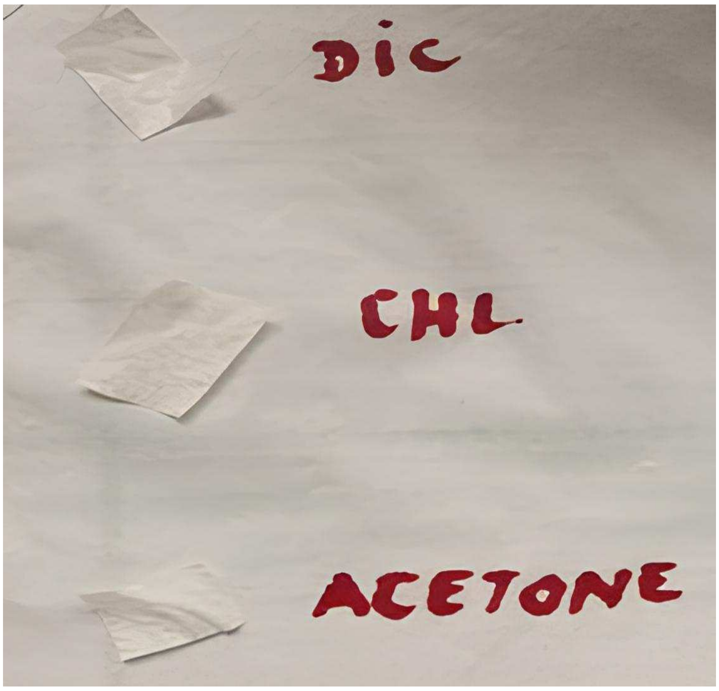

Fig. 5: Appearance of the membrane depending on the type of solvent with glycerol as plasticizer

Based on these observations, Chloroform/glycerol/CTA systems were retained for membrane fabrication with protocol 3. CTA concentrations were adjusted within the range of 15–17 wt% to ensure adequate mechanical integrity while avoiding excessive densification of the selective layer. Glycerol content was maintained between 8 and 12 wt% relative to CTA to enhance porosity and hydrophilicity while preserving structural stability. The resulting casting solutions exhibited consistent rheological behavior compatible with controlled film casting (wet thickness 180–220 µm), short air exposure times (25–40 s), and immersion in a water coagulation bath maintained at 20–23 °C, leading to reproducible asymmetric membrane morphologies with limited macrovoid formation. Optional mild hydrothermal annealing (50–60 °C, 30 min) was applied to further stabilize the selective layer and enhance ion rejection performance.

The chosen protocol was applied to commercial cellulose acetate sorting for a blank test before repeatability tests.

Fig. 6: Immersion precipitation phase for commercial cellulose acetate membranes

Repeatability tests indicated that chloroform-based formulations produced membranes exhibiting improved apparent mechanical robustness and structural integrity compared with other solvent systems.