

# Permeability of cellulose pulp membranes with nanocellulose

Angelo Cezar Lucizani<sup>1,2</sup>, Matheus Samponi Tucunduva Arantes<sup>2,3</sup>, Victor Verissimo Cardoso Lima<sup>2,3</sup>, Rosinaldo Rabelo Aparício<sup>1,2</sup>, Egon Petersohn Junior<sup>1,2</sup>, Oscar Giordani Paniz<sup>2</sup>, Washington Luiz Esteves Magalhães<sup>1,2</sup>, José Pedro Mansueta Serbena<sup>1</sup>

<sup>1</sup>Universidade Federal do Paraná, Programa de Pós-graduação de Engenharia e Ciência dos Materiais. Av. Cel. Francisco H. dos Santos, 100, Jardim das Américas, 81531- 980, Curitiba, PR, Brasil.

<sup>2</sup>Empresa Brasileira de Pesquisa Agropecuária, Embrapa Florestas, Centro de Tecnologia de Produtos Florestais, Laboratório de Tecnologia da Madeira. Estr. Da Ribeira – Br-476, 82630-148 Colombo, PR, Brasil.

<sup>3</sup>Universidade Federal do Paraná, Setor de Tecnologia, Programa de Pós-Graduação em Engenharia de Alimentos, Laboratório de Tecnologia de Alimentos. Av. Cel. Francisco H. dos Santos, 100, Jardim das Américas, 81530-000, Curitiba, PR, Brasil.

e-mail: angelo.lucizani@ufpr.br, matheussamponi@ufpr.br, victorverissimocl@gmail.com, rosinaldo.aparicio@ufpr.br, egondickens@gmail.com, oscar.paniz@hotmail.com, washington.magalhoes@embrapa.br, joseserbena@ufpr.br

#### **ABSTRACT**

In the quest to enhance filtration system performance and remove microscopic particles, researchers are increasingly interested in affordable materials made from renewable sources with low environmental impact. Cellulose stands out as one of the most promising materials due to its abundance in nature. In this study, we present a simple approach to manufacture cellulose foam with a microfibrillated cellulose (MFC) interface, intended to be used as a filter to capture airborne microparticles. Four different methods were employed to produce the membranes, aiming to analyze and compare the effectiveness of each process, including two distinct solvent exchange approaches and two solvent filtration techniques. Specifically, two membrane production methods were explored: (i) using water as a solvent, and (ii) employing acetone as a solvent. Regarding the solvent filtration process, two modalities were investigated: (i) natural filtration, and (ii) vacuum filtration. The MFC acted as reinforcement, promoting the formation of cross-links between the cellulose pulp fibers, thereby enhancing cellulose interfibrillar cohesion. An experimental system was utilized to assess pressure drop in a gas flow, and filter permeability was calculated. Overall, the membranes exhibited high permeability constants, emerging as a promising material for filtration processes.

Keywords: Cellulose foam; MFC; Filter; Permeability.

# 1. INTRODUCTION

The escalating global population has led to an augmented exploitation of natural resources and non-renewable sources, detrimentally impacting the quality of life for individuals. The consequential surge in air pollution, a direct outcome of this heightened activity, poses a significant threat to respiratory health. Environments with poor ventilation or exclusive reliance on air conditioning systems tend to harbor particulate-laden air, characterized by nanometric particles suspended in the atmosphere. This stagnant air exacerbates the risk of contamination, subsequently elevating the incidence of respiratory diseases. Delving into the realm of health-care, an imperative parallel emerges with the inadequacies in addressing contamination within hospital settings. A substantial number of healthcare facilities extensively employ air conditioning systems, often overlooking the potential intrahospital environment contamination. Several instances of hospital infections have been linked to the contamination of air conditioning filters by various biological agents, including fungi, bacteria, algae, mites, and viruses [1].

The magnitude and risks associated with air filter contamination become evident when examining outbreaks of endocarditis caused by Aspergillus sp. The link between these outbreaks and the contamination of air in cardiac surgery rooms, specifically attributed to spores originating from air conditioning unit filters, has been well-established<sup>2</sup>. Consequently, the use of high-quality filters with adequately sized pores becomes imperative to mitigate the risk of contamination.

Indoor filters commonly fall into two classifications: electrostatic filters and mechanical filters. While electrostatic filters, known as electrostatic precipitators, are highly efficient, their installation requires ample

Corresponding Author: Angelo Cezar Lucizani Received on 14/05/2024 Accepted on 19/08/2024

space, translating to a substantial initial investment [2–3]. On the other hand, mechanical filters, including panel filters, multi-bag filters, pleated filters, and HEPA filters [3], vary in efficiency and composition, typically consisting of microfiber tangles derived from synthetic (e.g., glass and polyester) or natural (e.g., charcoal and wood cellulose) fabrics [3–6].

Filtration, defined as the process of retaining particulates by a porous membrane, is integral to the reduction of nanometric particles. Fibrous filters, solid materials with pores, efficiently capture and accumulate particles, enhancing collection efficiency and reducing particle pressure. Cellulose, recognized as the most abundant renewable polymer, possesses desirable properties such as biodegradability, thermal and chemical stability, making it an excellent option for filtering materials [7–10].

Air filtration is the process of retaining particulate matter suspended in the gas stream. It is an essential element in the study of gas permeability. This procedure takes place in two ways, superficially and internally. In the internal filtration process, the cake formation mechanism occurs, in which the particulate is retained on the surface of the filter [11, 12]. Cake formation increases the efficiency of the filter, because as the particles are captured, they begin to retain new particles, i.e. these retained particles create a resistance to the flow, increasing the pressure drop and collection efficiency. In internal filtration, the particulates are retained in the pores inside the filter medium.

Cellulose is one of nature's most abundant raw materials, present in plants and some marine animals, and can be synthesized by some bacteria and fungi. This natural polymer is renewable, non-toxic, has low density, good mechanical properties, and is relatively inexpensive. Due to these numerous advantages, the use of this material has been growing in recent decades. Among the various applications attributed to cellulose are nanocellulose filters, biodegradable packaging reinforcement of composites and nanocellulose-based materials for removing contaminants from water [1–2, 4, 13]. Cellulose is a polysaccharide monomer, with a linear chain, composed of two anhydroglucose rings that are linked to each other through carbons 1-4, joined by glycosidic bonds of the  $\beta-(1\to 4)$  type, forming a cellobiose unit [5]. This natural polymer has the chemical structure  $C_6H_1O_5$ .

Nanocellulose is a material derived from the isolation of cellulose nanoparticles, in which at least one of the dimensions is smaller than 100 nm. This means that, on a nanoscale, cellulose particles are extremely small, allowing for unique properties and characteristics. While traditional cellulose is composed of macroscopic fibers visible to the naked eye, nanocellulose is made up of much smaller particles, giving it special properties such as high surface area and reactivity. This characteristic of diminutive size is what defines nanocellulose as a nanostructured material, enabling its application in a wide range of fields, including composite materials, biomaterials, and electronic devices. Nanocellulose, according to the literature, there are four main types of nanocellulose: microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), nanocrystalline cellulose (NCC) and bacterial cellulose (BNC). MFCs are about 10 – 100 nm in diameter; and as NFC, 500 – 200 nm; Cellulose nanocrystals (NCCs) have a diameter of 3 – 10 nm and a length of 50 – 500 nm [3–5, 13]. MFC and NFC, as they have alternating crystalline and amorphous regions, are in the form of a fiber network, and are flexible materials [5, 13]. NCCs have only crystalline regions, they are hydrolyzed cellulose nanoparticles, known as nanowhiskers or wiskers.

This study aims to investigate the filtration efficiency in filters produced with cellulose menbrane containing Microfibrillated Cellulose (MFC). Two methods of producing cellulose menbrane with MFC have been proposed, one involving solvent exchange and the other without solvent exchange, followed by drying in an oven at 60°C. Solvent exchange means the substitution of one solvent by other during membrane production. Permeability, a crucial parameter influencing fluid flow, will be evaluated using Fick's Law, considering factors such as porosity, filter structure, pore diameter, and suspended particle radius. Additionally, it will be investigated how permeability in clean membranes provides valuable insights into filter performance, leveraging the physical and mechanical properties of nanocellulose to increase filtration efficiency. These tests and evaluations of cellulose membrane will be compared with those conducted on HEPA filters. This comparison is essential to validate our experiments.

Cellulose, a semi-crystalline material, is by both crystalline and amorphous regions. The presence of crystalline regions acts as a limiting factor, reducing the material's permeability. When considering its application in filters, it is crucial for cellulose to exhibit meticulously controlled porosity, enabling the flow of air through its structure. Porosity, defined as the measure of empty space within a material, is a highly valued property in cellulose, as porous materials have the ability to facilitate the passage of substances, including liquids and gases [2–4, 13, 14–15]. The controlled porosity of cellulose plays a crucial role in various applications, such as in the production of filters, for example. The porosity of cellulose can be influenced by various factors, such as its intrinsic structure, the manufacturing method employed, and the treatment conditions



applied. In semi-crystalline polymers, crystalline regions tend to exhibit low permeability to gases due to their high crystallinity [2–4, 13–14]. For this reason, cellulose undergoes treatment processes aiming to increase its porosity and, consequently, its permeability, in order to be effectively used as a filtering material [2–4, 13, 14].

Based on the observed morphology of cellulose membrane with MFC, resembling randomly arranged glass fibers in a three-dimensional network [2–4, 13, 14], and the semi-crystalline nature of cellulose characterized by impermeable crystalline regions [5, 6, 13–15–17], our hypothesis is that filtration efficiency will be significantly enhanced with the incorporation of MFC nanocellulose layers in the filters. We believe that the high crystallinity and strong interfibrillar bonds of cellulose nanofibers will increase the capacity to retain suspended particles. Additionally, we expect that the choice of production method for cellulose membrane with MFC, whether with or without solvent exchange, will directly influence the filter's permeability, thus affecting its performance [5, 6, 13–17]. This hypothesis is grounded in Fick's Law and the understanding of factors such as porosity, filter structure, pore diameter, and suspended particle size, which play crucial roles in filtration efficiency [5, 6, 13–17].

The analysis of pore arrangement and permeability in clean membranes provides crucial insights into filter performance. Therefore, the physical and mechanical properties of nanocellulose have garnered considerable interest among researchers, given its wide range of industrial applications. The incorporation of cellulose paste with MFC aims to enhance filtration efficiency by leveraging the unique characteristics of this material.

## 2. MATERIALS AND METHODS

## 2.1. Materials

Bleached and dried commercial cellulose pulp was kindly donated by Brazilian company Klabin. Commercial air conditioner HEPA filter (Electrolux) was purchased and used as comparative baseline for the developed membranes in this work. High-grade acetone (92.0 – 92.5 wt.%, Alphatec, Brazil) and distilled water were used as solvents in the preparation of the membranes.

## 2.2. Nanocellulose modification of membranes

Given the initially low permeability of the membranes, impeding the desired airflow, various pre-treatments were employed to enhance their performance. Specifically, these membranes underwent a process to introduce nanopores while maintaining yet ensuring adequate air permeability [18–20]. The nanocellulose played a crucial role as an interface for the cellulose membrane, establishing an extensive hydrogen bonding network. It acted as fibrillar bridges, facilitating crosslinking between fibers to improve the fiber-fiber bond between cellulose fibers and cellulose-nanocellulose fibers [19, 20]. Microfibrillated cellulose suspension (MFC) was produced by a physical process, with the defibrillation of the commercial cellulose pulp (approximately 25 g) in distilled water (approximately 3 L) using a colloid mill (MKCA6-2J Super Masscoloider, Masuko Sangyo) in which the mixture underwent mechanical homogenization. After prepared, the MFC suspension was stored in plastic bottles until further use.

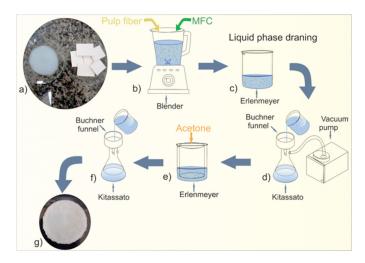
#### 2.3. Preparation of cellulose pulp/MFC membrane

Initially, the MFC suspension was mixed with commercial cellulose pulp, and the mixture (approximately 200 g) was homogenized in a laboratory blender for 5 min. The material was used to produce the pulp/MFC membranes, which was conducted as summarized in Figure 1 with different methodologies. Two key parameters on the membranes production methodology were evaluated: the water excess removal (natural filtration versus vacuum filtration), and a solvent exchange additional step (no solvent exchange versus water-to-acetone solvent exchange). The details of the production of each sample are presented in Table 1.

For the natural filtration method, the suspension (500 mL) was transferred to a Büchner funnel with a nylon membrane, and it was allowed to rest for the total filtration time of 2 h. On the other hand, in the vacuum filtration process, the suspension (500 mL) was also transferred to a Büchner funnel with a nylon membrane, connected to a Büchner flask coupled to a vacuum pump, with a filtration time of approximately 15 min. Membranes obtained without solvent exchange underwent a single filtration process, and the resulting membranes were collected. In the case of membranes subjected to water-acetone solvent exchange, after the initial filtration process, the membranes were immersed in acetone for 30 min. Subsequently, the suspension underwent a second filtration process, and the resulting membrane was collected.

All collected membranes were placed in a freezer at  $-18^{\circ}$ C for 12 h and thawed at room temperature before being dried in an oven at  $60^{\circ}$ C. Freezing is employed to reorganize the fibers, facilitating fiber crosslinking during ice crystal formation. This process resulted in an irregular 3D porous network, achieved by pressing the





**Figure 1:** Pulp membrane preparation process with MFC. a) MFC and cellulose; b) process of mixing cellulose pulp with MFC; c) liquid drainage; d) Vacuum processing and filtration; d) soaking the cellulose pulp/MFC; natural filtration process; f) Filtration process; g) cellulose pulp/MFC filter.

**Table 1:** It shows the methodology used to produce the membranes.

*SAMPLE	WATER REMOVAL	SOLVENT EXCHANGE***	MFC (%)
**HEPA	_	_	_
NF-NSE-04	natural filtration	No	0.4
VF-NSE-08	vacuum filtration	No	0.8
NF-NSE-08	natural filtration	No	0.8
NF-NSE-04	vacuum filtration	No	0.4
NF-YSE-04	natural filtration	Yes	0.4
VF-YSE-04	vacuum filtration	Ye	0.4
NF-YSE-08	natural filtration	Yes	0.8

<sup>\*</sup>NF-NSE: natural filtration no solvent Exchange; NF-YSE: natural filtration yes solvente Exchange; VF-NSE: vacuum filtration no solvent Exchange yes solvente Exchange. \*\*Commercial HEPA filter; \*\*\*Water exchanged to acetone.

fibers into a geometry similar to randomly oriented 2D sheet during freezing. This process yielded the P/FMC membranes, which were utilized in subsequent tests. The variation in water removal rates aimed to assess whether faster or slower water removal would yield a greater quantity of pores. After the drying process, the nylon membrane was manually removed from the pulp/MFC membranes with care to avoid damaging the sample. Samples were stored separately in plastic bags at room temperature  $(20 - 25^{\circ}C)$  until further analyses.

## 2.4. Characterization

# 2.4.1. Permeability

The permeability coefficient serves as a macroscopic indicator of viscous resistance, providing information on the ease of flow of a fluid through a porous medium [21–22]. In this study, the permeability coefficients (P m²) of the filters developed were determined using a system designed by the authors (Figure 2) and the calculations were based on Fick's Law (Equation 1)

$$j = P\left(\frac{\Delta p}{l}\right) \tag{1}$$

where J (m<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup>) is the air flow, l (m) represents the filter thickness, and  $\Delta p$  (Pa) is the pressure variation in the water column, given by Equation 2 [22–23].



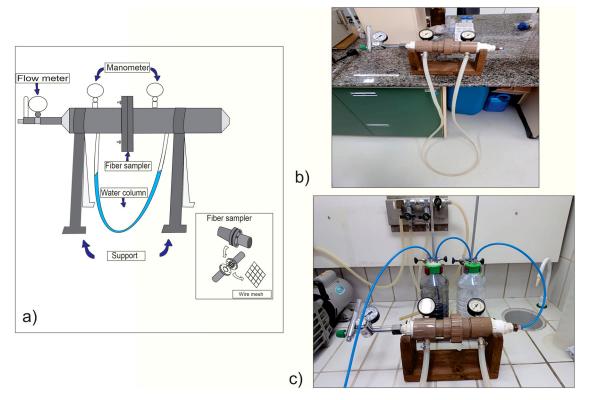


Figure 2: Equipment for permeability testing. a) Equipment design; b) Equipment for permeability tests; c) Equipment with particle tube.

$$\Delta \mathbf{p} = \tilde{\mathbf{n}} \cdot \mathbf{G} \cdot \Delta \mathbf{h} \tag{2}$$

where  $\rho$  (997 kg m<sup>-3</sup>) is the density of water, g (9.8 m s<sup>-2</sup>) is the acceleration due to gravity [23], and  $\Delta h$  (m) is the height variation of the water column. The flux through the membrane is given by Equation 3.

$$j = \frac{Q}{A} \tag{3}$$

where  $Q_c$  (m³ s¹) is the corrected flow rate and A (m²) is the transversal area of the filter. Rotameters were used to measure air flow. It was necessary to make a correction to the air flow rate, as it was not in the same condition to carry out the experiments. The corrections were in relation to pressure and temperature [23], as shown in Equation 4.

$$Q_{c} = Q_{m} \cdot \sqrt{\frac{\tilde{n}_{o}}{\tilde{n}_{c}}} \cdot \sqrt{\frac{T_{c}}{T_{o}}}, \tag{4}$$

where  $Q_c$  is the corrected flow rate,  $Q_m$  is the measured flow rate,  $p_o$  is the operating pressure,  $p_c$  is the calibration pressure,  $T_c$  is the calibration temperature and  $T_o$  is the operating temperature. The calibration measurements were used under normal temperature and pressure conditions. Fick's Law [22] is then expressed as Equation 5.

$$P = \frac{Q_c}{A} \cdot \frac{e}{\Delta p} \tag{5}$$

In the experimental setup, a controlled synthetic air stream at controlled pressure was introduced toward the filter. A flow meter measured the stream flow, while chambers before and after the filter were connected by a hose partially filled with water. For each flow value  $(2 - 10 \text{ L min}^{-1})$ , the pressure drop was calculated according to Equation 3.

## 2.4.2. Apparent density and porosity

The apparent density  $\rho_{ap}$  and bulk density  $\rho s$ , was calculated by the ratio of the mass of the dry membrane to the volume, i.e., of a density material is defined as the mass of the material divided by its total volume, including any pore space or voids. Considering that the density of the cellulose pulp ( $\rho p$ ) is 1.46 g/cm<sup>3</sup> [23–28]. Porosity is calculated according to Equation 7.

$$P(\%) = \left(\frac{\tilde{n}_{ap}}{\tilde{n}_{s}}\right).100. \tag{6}$$

## 2.4.3. Mechanical properties

The Q800 DMA equipment was used to analyze the dynamic-mechanical properties (DMA) and were used to determine the mechanical performance of the membrane. The membranes were subjected to a compression test. A constant temperature was used in this test.

#### 2.4.4. Determination of surface area

A Quantachrome Instruments equipment (NOVA 1200e) was utilized on the determination of the specific surface area of each filter. The filters were previously dried at an oven (60°C, 12 h) and degassed (100°C, 2 h). Then, nitrogen adsorption/desorption processes were carried at -196°C and the Brunauer, Emmet and Teller (BET) method was adjusted to the adsorption data.

#### 2.4.5. Experimental unit

The permeability of the filters was assessed using a system devised by the authors, as illustrated in Figure 2. Within this system, a controlled synthetic air stream maintaind at a specific pressure, was introduced toward the filter. A flow meter was employed to measure the stream flow accurately. The chambers located before and after the filter were connected by a hose partially filled with water. For each flow value (2–6 and 10 l min<sup>-1</sup>), the pressure drop across the filter measured and calculations were carried out as per Equation 4. Subsequently. A graph depicting the relationship between pressure drop and stream flow was plotted. The angular coefficient obtained from the linear adjustment of this data was utilized to determine the permeability coefficient for each filter. This method provides a comprehensive understanding of the filters' performance in terms of fluid flow resistance.

#### 2.4.6. Particle retention tests

Filtration tests were conducted using a compressed air line and specialized particle loss or filtration equipment. The experimental filtration system employed for these tests is detailed in Figure 2. The system included two pressure gauges, positioned at the inlet and outlet, along with a water column to asses the pressure drop. To prevent the nanocellulose film from escaping a metal screen was affixed to the fiber sampler. A constant flow system was established using an injection pump, ensuring a consistent pressure of the percolating fluid at both the inlet and outlet of the test body. The membrane, serving as the filter media, was placed into the filtration support, and the gas stream then traversed through the porous material during the test. This setup allowed for precise examination of the membranes efficacy in retaining particles and provided valuable data on its filtration performance.

## 3. RESULTS AND DISCUSSION

Previous works focused on the obtention of membranes from nanocellulose usually report that the membranes obtained through the conventional oven drying of nanocellulose suspensions dispersed in water present low permeability, resulting in difficulties for the air transport. Additionally, authors suggest that the membranes that present nanopores can maintain a low porosity, but with adequate air permeability [23–26]. In the current work, the nanocellulose served as an interface for cellulose membranes, providing an extensive hydrogen bonding network. In other words, it served as fibrillar bridges, forming crosslinking between the fibers [18–20, 26, 27–29, 30–33], in order to improve the fiber-fiber bond between the cellulose fibers and the cellulose-nanocellulose fiber. In order to enlarge the pores and increase the membranes permeability. From these data, it was possible to determine the permeability constant, which was obtained through Equation 5. To do so, it was necessary to construct the permeability curve (ΔP/l versus v), presented in Figure 3.

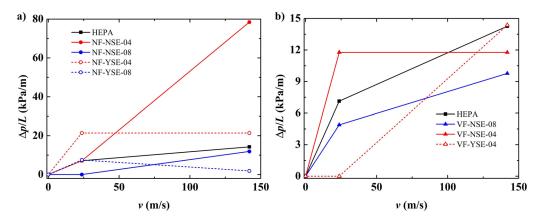


Figure 3: a) Pressure drop curves as a function of velocity for samples natural filtration; b) Pressure drop curves as a function of velocity for samples natural vacuum.

<b>Table 2:</b> Presents the permeability	constants. P1 is the initial pressure.
---	--

SAMPLE	P (m <sup>2</sup> )
HEPA	6.63 × 10 <sup>-3</sup>
NF-NSE-04	5.20 × 10 <sup>-4</sup>
VF-NSE-08	6.63 × 10 <sup>-3</sup>
NF-NSE-08	8.34 × 10 <sup>-4</sup>
VF-NSE-04	$1.66 \times 10^{-2}$
NF-YSE-04	$2.84 \times 10^{-2}$
VF-YSE-04	$1.19 \times 10^{-2}$
NF-YSE-08	$7.81 \times 10^{-3}$

For control tests, the HEPA filter (HEPA) was used to compare with the samples produced. The membranes obtained practically the same behavior as the HEPA filter, as can be seen in Figure 3.a and figure 3.b. It is observed that the pressure drop maintained a relatively constant trend as the air stream speed increased. As predicted, there was no significant increase in pressure drop, as the filtration process occurred without the presence of particles, indicating the ease of fluid passage through the pores. This test analyzed the relationship between the pressure drop and the increase in surface air velocity in the filtration line. In this test, only compressed air was circulating in the filtration equipment and no particles were present. Thus, the filtration speed varied from  $2.0 \times 10^1$  m/s an  $2.5 \times 10^3$  m/s, and the flow rate varied from 2 l/min, 6 l/min and 10 l/min. The pressure drop data was acquired from the water column, as shown in figure 2. With this data, it was possible to determine the permeability constant, obtained using the equation 5. The permeability coefficient serves as a macroscopic indicator of viscous resistance, providing information on the ease of flow of a fluid through a porous medium [16, 17, 21, 28].

These tests were carried out with different membranes, as shown in Table 2. The results of the permeability tests of the filters without the presence of particles, known as clean filters, were obtained from data from the equation 5 and showed values very close to each other (Table 2). Among the membranes, membranes NF-NSE-04, NF-NSE-08, NF-YSE-04 and NF-YSE-08 showed the best results for the permeability constant, with  $10^{-4}$ m², showing that solvent exchange and natural filtration are better options. As for increasing the amount of MFC, there wasn't much change, so that 0.4% gel is enough to obtain a porous membrane. For more permeable membranes, surface filtration is more significant, since the lower the permeability constant, the greater the capacity to retain particles on its surface. According to Table 1, the samples that were dried naturally and with solvent exchange had better results in terms of permeability constants compared to the HEPA filter.

The results obtained by BET analysis showed that membranes VF-NSE-08 and VF-NSE-04 had a small difference in surface area. For membranes NF-NSE-04 and NF-NSE-08, which had the water removed naturally, the values were similar, as shown in Table 2. The samples that underwent solvent exchange and had the solvent removed naturally exhibited a relatively high surface area compared to the other membranes, as observed in Figure 4. The results are shown in Table 2. These values are lower compared to some values found in the literature. To increase the material's surface area, alternative drying strategies, such as freeze-drying, can be



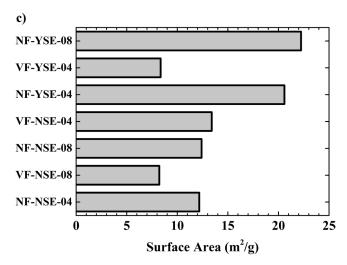


Figure 4: Surface area of the membrane.

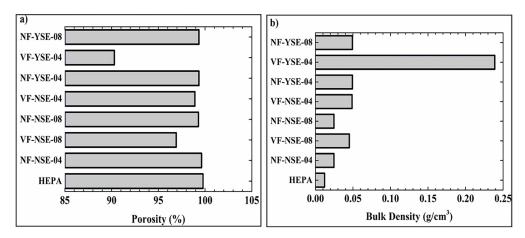


Figure 5: a) shows a graph of the porosity of each membrane; b) shows a graph of the apparent density of each membrane.

utilized, potentially leading to higher surface area values. However, this would result in increased production costs. In our research, we sought low-cost processes. Therefore, despite the lower values, the membranes remain excellent options for use as filters.

The apparent density and porosity are shown in the figure 5.a and figure 4.b. membranes NF-NSE-04, NF-NSE-08, NF-YSE-04 and NF-YSE-08 showed high porosity and low density. This was due to the way the membranes were filtered, as the longer the filtering time, the greater the porosity. As the nanocellulose content increased, the pores decreased, because the nanocellulose ended up occupying the pores, and consequently the solid cellulose increased. Similar tests were carried out, however, to analyze the retention of the particles in the membrane. We deposited silica nanoparticles in the air stream, as shown in figure 1. The efficiency of the membranes ranged from 90% to 99.8%, as shown in the figure 3. this test showed a comparison of the different pre-treatments, with the reaction between the porosity (figure 5.a) and the apparent density (figure 5.b). Membranes NF-NSE-04, NF-NSE-08, NF-YSE-04 and NF-YSE-08 showed high porosity and low density. This was due to the way the membrane was filtered, as the longer the filtering time, the greater the porosity.

As the nanocellulose content increased, the pores decreased, because the nanocellulose ended up occupying the pores, and consequently the solid cellulose increased. The Figure 6, shows the results of the stress-strain curves, showing excellent mechanical properties with a compressive stress of 0–0.9 MPa at 60% strain for sample NF-NSE-08 . Samples VF-NSE-08, NF-YSE-04 and VF-YSE-04 showed deformation of less than 30%.

To characterize the membranes and obtain information about the surface such as topology, scanning electron microscopy (SEM) was used. The way the membrane is filtered also influences the crosslinking, as shown in Figure 7. We can see in Figure 6 that the membranes showed good crosslinking of the cellulose pulp with the MFC. As can be seen in Figure 7, there was a small difference in morphology between the methodologies

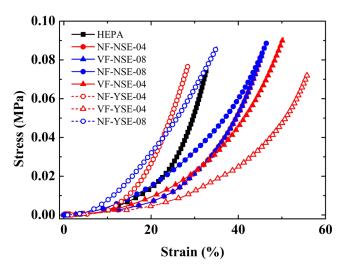
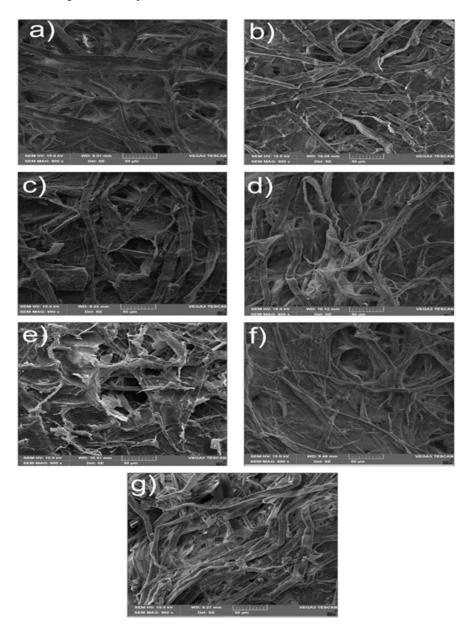


Figure 6: Stress-strain diagrams for compression of cellulose membranes.



**Figure 7:** Shows the images obtained by scanning electron microscope (SEM) of the membranes in 900x; a) NF-NSE-04; b) VF-NSE-08; d) VF-NSE-04; e) NF-YSE-04; f) VF-YSE-04; g) NF-YSE-08.



used. The use of methodologies showed an increase in pores in the material structure and fiber entanglement. Most membranes had the potential to be used as filters. The fibers in both samples were on the nanometer scale of the membranes.

The authors related the examined parameters to the results of the HEPA filter. As a result, they concluded that the membranes made from cellulose pulp with MFC demonstrated an effective capacity for particle retention. Specifically, the samples that underwent the natural filtration process and solvent exchange (NF-NSE-04, NF-NSE-08, NF-YSE-04) exhibited the best performances, achieving values comparable to those obtained with the HEPA filter, as evidenced by the results.

The substitution of the solvent played a crucial role in the membrane fabrication process, as the objective was to obtain a porous material to increase permeability. The selection of a more volatile solvent, such as acetone, was essential in inducing the formation of greater porosity, directly impacting the desired properties of the material. Solvent derived from biomass was not utilized, as this approach had been previously explored in existing literature, prompting the decision to opt for acetone. The higher volatility of acetone compared to alcohol, for example, was one of the factors taken into consideration in this choice.

The production of cellulose pulp membranes as a material for filtration is in compliance with various principles of green chemistry, as proposed by Szekely [34]. Cellulose, due to its renewable origin and environmentally friendly degradability, aligns with the principle of using renewable materials (principle 8). The application of these membranes in filtration processes can promote atomic efficiency (principle 2) by allowing selective separation of substances, reducing the need for additional chemical processes, and minimizing waste. Additionally, drying in a 60°C oven may impact the principle of more efficient energy use (principle 6), while also contributing to waste prevention (principle 1) by enabling the purification and separation of substances in a more efficient and sustainable manner [34–36].

For future tests, we plan to produce membranes using different solvents and also dry the samples using the lyophilization method. These additional steps have the potential to provide valuable insights and enhance the quality of the results obtained in our research.

#### 4. CONCLUSIONS

According to the results obtained, and the efficiency tests of the filter medium, it was possible to conclude that the methodology and pre-treatments used to produce cellulose membrane with MFC can be used as a filter. Comparing the pre-treatments, the f that showed the best results were those with solvent exchange and without the use of the vacuum pump. This technique causes the formation of bridges between the fibrils, as can be seen in the SEM images, resulting in the production of pores. The permeability values obtained show that the membranes are a material with great potential for use as filters for removing nanoparticles. The results of the permeability constants were between  $10^{-2}$  and  $10^{-4}$  m<sup>2</sup>, showing high permeability, compatible with European and Brazilian standards.

## 5. ACKNOWLEDGMENTS

The authors would like to thank the financial support from the Coordination for the Improvement of Higher Education Personnel (CAPES) – Notice No. 9/2020 for Emergency Selection I – Prevention and Combat of Outbreaks, Endemics, Epidemics and Pandemics of the CAPES-EPIDEMIAS Program; Federal University of Parana; Wood Technology Laboratory at Embrapa Florestas de Colombo- Pr; The company Klabin for the supply of cellulose.

#### 6. BIBLIOGRAPHY

- [1] DANTAS, E.H.M., "Ar condicionado, vilão ou aliado? Uma revisão crítica", *Revista Brasindoor*, v. 2, n. 9, pp. 4–9, 1998.
- [2] NOLARD, N., "Les liens entre les risques d'asdpergillose et la contamination de l'environnement", *Pathologie Biologie*, v. 7, pp. 706–710, 1994. PubMed PMID: 7877866.
- [3] MOON, R.J., MARTINI, A., NAIRN, J., *et al.*, "Cellulose nanomaterials review: structure, properties and nanocomposites", *Chemical Society Reviews*, v. 40, n. 7, pp. 3941–3994, 2011. doi: http://doi.org/10.1039/c0cs00108b. PubMed PMID: 21566801.
- [4] DUFRESNE, A., "Nanocellulose processing properties and potential applications", *Current Forestry Reports*, v. 5, n. 2, pp. 76–89, 2019. doi: http://doi.org/10.1007/s40725-019-00088-1.

- [5] NECHYPORCHUK, O., PIGNON, F., BELGACEM, M.N., "Morphological properties of nanofibrillated cellulose produced using wet grinding as an ultimate fibrillation process", *Journal of Materials Science*, v. 50, n. 2, pp. 531–541, 2015. doi: http://doi.org/10.1007/s10853-014-8609-1.
- [6] SYVERUD, K., STENIUS, P., "Strength and barrier properties of mfc filmes", *Cellulose (London, England)*, v. 75, n. 16, pp. 75–85, 2009. doi: http://doi.org/10.1007/s10570-008-9244-2.
- [7] BRITISH STANDARD, High efficiency air filters (epa,hepa and ulpa), Londres, Reino Unido, BS, 2009.
- [8] PEER, P., JANALIKOVA, M., SEDLARIKOVA, J., *et al.*, "Antibacterial filtration membranes based on PVDF-co-HFP nanofibers with the addition of medium-chain 1-monoacylglycerols", *ACS Applied Materials & Interfaces*, v. 13, n. 34, pp. 41021–41033, 2021. doi: http://doi.org/10.1021/acsami.1c07257. PubMed PMID: 34405995.
- [9] WANG, B., WANG, Q., WANG, Y., *et al.*, "Flexible multifunctional porous nanofibrous membranes for high-efficiency air filtration", *ACS Applied Materials & Interfaces*, v. 11, n. 46, pp. 43409–43415, 2019. doi: http://doi.org/10.1021/acsami.9b17205. PubMed PMID: 31659893.
- [10] SEM WANG, C., et al., "Removal of nanoparticles from gas streams by fibrous: a review", *Industrial & Engineering Chemistry Research*, v. 75, n. 16, 2013.
- [11] BORTOLASSI, A.C.C., GUERRA, V.G., AGUIAR, M.L., "Characterization and evaluate the efficiency of different filter media in removing nanoparticles", *Separation and Purification Technology*, v. 175, pp. 79–86, 2017. doi: http://doi.org/10.1016/j.seppur.2016.11.010.
- [12] KALAYCI, V., OUYANG, M., GRAHAM, K., "Polymeric nanofibres in high efficiency filtration applications", *FILTRATION-COALVILLE*, v. 6, n. 4, pp. 286, 2006.
- [13] NAIR, S.S., ZHU, J.Y., DENG, Y., *et al.*, "Characterization of cellulose nanofibrillation by micro grinding", *Journal of Nanoparticle Research*, v. 16, n. 4, pp. 1–10, 2014. doi: http://doi.org/10.1007/s11051-014-2349-7.
- [14] ZHANG, J., CHOI, Y.S., YOO, C.G., et al., "Cellulose-hemicellulose and cellulose-lignin interactions during fast pyrolysis", ACS Sustainable Chemistry & Engineering, v. 3, n. 2, pp. 293–301, 2015. doi: http://doi.org/10.1021/sc500664h.
- [15] SONG, J., ZHANG, B., LU, Z., *et al.*, "Hierarchical porous poly (l-lactic acid) nanofibrous membrane for ultrafine particulate aerosol filtration", *ACS Applied Materials & Interfaces*, v. 11, n. 49, pp. 46261–46268, 2019. doi: http://doi.org/10.1021/acsami.9b18083. PubMed PMID: 31718154.
- [16] WASHBURN, E. W. *Note on a method of determining the distribuition of pores sizes in a porus material*, 1921. accessed in https://api.semanticscholar.org/CorpusID:20262396, August, 2024.
- [17] WASHBURN, E.W., "Study of porosity and permeabillity of air filter material in respiratory protection filters", In: *Processeding of the National Academy of the United States of America*, pp. 115–116, 1921
- [18] CHEN, Y., JIANG, Y., WAN, J., *et al.*, "Effects of wet-pressing induced fiber hornification on hydrogen bonds of cellulose and on properties of eucalyptus paper sheets", *Holzforschung*, v. 72, n. 10, pp. 829–837, 2018. doi: http://doi.org/10.1515/hf-2017-0214.
- [19] FNEICH, F., VILLE, J., SEANTIER, B., *et al.*, "Nanocellulose-based foam morphological, mechanical and thermal properties in relation to hydrogel precursor structure and rhheoogy", *Carbohydrate Polymers*, v. 253, n. 117233, pp. 117233, 2021. doi: http://doi.org/10.1016/j.carbpol.2020.117233. PubMed PMID: 33278990.
- [20] SUN, L., LIU, L., WU, M., *et al.*, "Nanocellulose interface enhanced all-cellulose foam with controllable strength via a facile liquid phase exchange route", *Carbohydrate Polymers*, v. 299, pp. 120192, 2023. doi: http://doi.org/10.1016/j.carbpol.2022.120192. PubMed PMID: 36876806.
- [21] SHEMER, H., SAGIV, A., HOLENBERG, M., et al., "Filtration characteristics of threaded microfiber water filters", *Desalination*, v. 431, pp. 80–85, 2018. doi: http://doi.org/10.1016/j.desal.2017.07.009.
- [22] HABERT, A.C., Processo de separação com membranas, Rio de Janeiro, Editora, 2006.
- [23] ZHU, Y., ZHU, J., YU, Z., *et al.*, "Air drying scalable production of hydrophobic, mechanically stable, and thermally insulating lignocellulosic foam", *Chemical Engineering Journal*, v. 450, n. 138300, pp. 3, 2022. doi: http://doi.org/10.1016/j.cej.2022.138300.
- [24] LI, J., YANG, X., XIU, H., *et al.*, "Structure and performance control of plant fiber based foam material by fibrillation via refining treatment", *Industrial Crops and Products*, v. 128, pp. 186–193, 2019. doi: http://doi.org/10.1016/j.indcrop.2018.10.085.

- [25] FERREIRA, E.S., REZENDE, C.A., "Simple preparation of cellulosic lightweight materials from eucalyptus pulp", *ACS Sustainable Chemistry & Engineering*, v. 6, n. 11, pp. 14365–14373, 2018. doi: http://doi.org/10.1021/acssuschemeng.8b03071.
- [26] FERREIRA, E.S., CRANSTON, E.D., REZENDE, C.A., "Naturally hydrophobic foams from lignocellulosic fibers prepared by oven-drying", *ACS Sustainable Chemistry & Engineering*, v. 8, n. 22, pp. 8267–8278, 2020. doi: http://doi.org/10.1021/acssuschemeng.0c01480.
- [27] ANTONINI, C., WU, T., ZIMMERMANN, T., et al., "Ultra-porous nanocellulose foams: a facile and scalable fabrication approach", *Nanomaterials (Basel, Switzerland)*, v. 9, n. 8, pp. 1142, 2019. doi: http://doi.org/10.3390/nano9081142. PubMed PMID: 31404987.
- [28] LEE, H., KIM, S., SHIN, S., et al., "Structure of lighweight, conductive cellulose nanofiber foam", *Carbohydrate Polymers*, v. 253, pp. 117238, 2021. doi: http://doi.org/10.1016/j.carbpol.2020.117238.
- [29] LACERDA, M.P., et al., "Effect of adding nanofibrillated cellulose pulp on the properties of coating mortars", *Matéria (Rio de Janeiro)*, v. 28, n. 2, pp. e20230063, 2023. http://doi.org/10.1590/1517-7076-rmat-2023-0063.
- [30] FATIMA, A., ORTIZ-ALBO, P., NEVES, L.A., *et al.*, "Biosynthesis and characterization of bacterial cellulose membranes presenting relevant characteristics for air/gas filtration", *Journal of Membrane Science*, v. 674, pp. 121509, 2023. doi: http://doi.org/10.1016/j.memsci.2023.121509.
- [31] HARDIAN, R., ALAMMAR, A., HOLTZL, T., *et al.*, "Fabrication of sustainable organic solvent nanofiltration membranes using cellulose-chitosan biopolymer blends", *Journal of Membrane Science*, v. 658, pp. 120743, 2022. doi: http://doi.org/10.1016/j.memsci.2022.120743.
- [32] ABDELLAH, M.H., OVIEDO, C., SZEKELY, G., "Controlling the degree of acetylation in cellulose-based nanofiltration membranes for enhanced solvent resistance", *Journal of Membrane Science*, v. 687, pp. 122040, 2023. http://doi.org/10.1016/j.memsci.2023.122040.
- [33] TRAN, D.H., ULBRICHT, M. "Cellulose-cellulose composite membranes for ultrafiltration", *Journal of Membrane Science*, v. 672, pp. 121426, 2023. doi: http://doi.org/10.1016/j.memsci.2023.121426.
- [34] SZEKELY, G., "The 12 principles of green membrane materials and processes for realizing the United Nations' sustainable development goals", *RSC Sustainability*, v. 2, n. 4, pp. 871–880, 2024. doi: http://doi.org/10.1039/D4SU00027G.
- [35] CORRÊA, A.C., et al., "Cellulose nanofibers from curuau fiber", Cellulose (London, England), v. 17, n. 1, pp. 11883–1192, 2010.
- [36] KLEMM, D., KRAMER, F., MORITZ, S., et al., "Nanocelluloses: a new family of nature-based materials", *Angewandte Chemie International Edition in English*, v. 50, n. 24, pp. 5438–5466, 2011. doi: http://doi.org/10.1002/anie.201001273. PubMed PMID: 21598362.