Hybrid Polyamide Membranes Obtained by the Immersion Precipitation Method

Joanne Graziela Andrade Mendes[1*], Damares Oliveira de Jesus Ferreira[1], Airan Magalhães Moura[1], Carlos Antônio Pereira de Lima[2], Arthur de Sousa Ferreira[2], Keila Machado de Medeiros[1]
[1]Center for Science and Technology in Energy and Sustainability, Federal University of Recôncavo of Bahia; Feira de Santana, Bahia; [2]Department of Sanitary and Environmental Engineering, State University of Paraíba; Campina Grande, Paraíba, Brazil

This research explores replacing petrochemical derivatives with renewable resources, focusing on developing natural fiber composites. Hybrid membranes composed of polyamide 6 and sodium hydroxide-treated sisal fiber were fabricated using immersion precipitation. The membranes were analyzed for water absorption, porosity, permeability fluxes, and yield. Results indicate that the fiber content influences porosity and pore radius. Pure membranes and those containing 1% fiber exhibited higher porosity than those with 3% and 0.33% fiber. All membranes demonstrated high dye removal efficiency, achieving yields above 95%. The study concludes that incorporating sisal fiber enhances the membrane properties, making them highly effective for textile dye separation and microfiltration applications.

Keywords: Membrane. Sisal Fiber. Polyamide 6. Immersion Precipitation. Dye Removal.

The exploration of renewable resources as alternatives to petrochemical derivatives has garnered significant attention due to their environmental benefits. Among these alternatives, composites reinforced with natural fibers have demonstrated outstanding potential for various applications [1].

Natural fibers exhibit mechanical properties that enhance the characteristics of polymer matrices, making them a viable choice for reinforcement [2]. Commonly used natural fibers include sisal, coconut, bamboo, and banana. In Brazil, fibers such as jute, banana, piassava, sugarcane, coconut, sisal, and cotton dominate the market, accounting for 93% of national production [3]. Sisal fiber, in particular, offers advantages such as low cost, biodegradability, and non-toxicity [4]. However, the size and processing of these fibers significantly influence the resulting composites' properties by affecting dispersion and membrane morphology.

Sisal fiber is notable for its mechanical strength, although it is hydrophilic compared to other natural fibers. When incorporating hydrophilic fibers into hydrophobic polymers, surface treatments are often required to enhance interfacial adhesion and improve mechanical performance—key factors for producing high-quality composites [5]. Chemical and physical surface treatments can enhance the interaction between sisal fiber and polymer matrices, improving the mechanical properties of reinforced membranes. These properties are influenced by fiber/matrix adhesion, the volume fraction of fibers, and their dispersion within the matrix [6].

Membrane separation processes (MSPs) have diverse applications in the medical, biological, and pharmaceutical fields, as well as in the chemical and food industries [3]. The phase inversion method is desirable due to its simplicity, cost-effectiveness, and efficiency in preparing symmetric and asymmetric microporous membranes [2].Polyamides, known for their excellent abrasion resistance and thermal stability, are commonly used with natural fibers like sisal to produce polymer composites with enhanced properties.

This study aims to develop hybrid membranes of polyamide 6 and sodium hydroxide-treated sisal fiber fabricated using immersion precipitation.

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Address for correspondence: Joanne Graziela Andrade Mendes. Av. Centenário, 697 - Sim, Feira de Santana - BA, Brazil, Zipcode: 44042-280. E-mail: mendesanne736@gmail.com.

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Materials and Methods

Preparation of Treated Sisal Fiber

Sisal fiber was used in three proportions—0.33%, 1.0%, and 3.0%—to prepare hybrid membranes. The fibers underwent a surface treatment involving immersion in a 3.0% sodium hydroxide solution for 1 hour. Following the treatment, the fibers were thoroughly rinsed in distilled water baths until a neutral pH was achieved. The neutralized fibers were then dried in an oven at 80°C for 24 hours to remove residual moisture.

Membrane Fabrication

Polyamide 6 (PA6), coded as Technyl® C216, with an average molar mass of 10,500 g/mol and intrinsic viscosity (IV) of 134 mL/g, supplied by Rhodia/SP, served as the polymer matrix. PA6 pellets and hybrid mixtures containing 0.33%, 1.0%, and 3.0% (by weight) of treated sisal fiber were dissolved in hydrochloric acid to prepare the membranes. The solutions underwent homogenization for 4 hours at room temperature to ensure uniform dispersion of the fibers.

Membrane Characterization Water Absorption Capacity

Water absorption capacity was evaluated by immersing the membranes at 24°C for 48 hours. The test was conducted in triplicate for accuracy.

Porosity

Membrane porosity was determined by immersing the membranes in water for 48 hours. Measurements included the initial membrane mass, the amount of water absorbed, the volume of the membranes, and the density of water.

Pore Radius

The mean pore radius of the membranes was calculated using the Guerout-Efford-Ferry equation, which correlates porosity and other physical parameters.

Permeability Flux

Continuous flow experiments were performed using a perpendicular filtration cell under a constant pressure of 1.0 bar. To measure permeability, filtrate samples were collected at 1-minute intervals for a total duration of 60 minutes.

Textile Dye Removal Efficiency

The membranes' capacity to remove textile dyes was evaluated using ultraviolet-visible spectroscopy. These analyses were conducted at the Materials Characterization Laboratory of the Center for Science and Technology in Energy and Sustainability, Federal University of Recôncavo of Bahia.

Results and Discussion

Water Absorption and Porosity

Figure 1 (a) illustrates the water absorption, and Figure 1 (b) shows the porosity of the pure PA6 membranes and hybrids with 0.33%, 1%, and 3% sisal fiber.

The retention capacity of a membrane is influenced by its porosity, which can either expand or improve permeability. Figure 1 shows that, in general, water absorption decreases with increasing fiber content. In the porosity analysis, a membrane obtained by immersion precipitation is mainly influenced by phase separation, responsible for membrane formation and pore distribution. Figure 1(b) shows that the pure PA6 membrane and the PA6 membrane with 1% sisal fiber present greater porosity than those containing 3% and 0.33% fiber, following the exact water absorption behavior. Adding 1% fiber promoted the best water absorption and porosity results. However, a high concentration of fibers, as in the membranes with 3% sisal, led to agglomeration and reduced porosity. This behavior can be explained by the surface treatment performed on the fiber, which aims to improve the filler/matrix interface. Applying aqueous sodium hydroxide (NaOH(aq)) on the sisal fiber causes the ionization of the hydroxyl group into an alkoxide. With the reduction of the hydrophilic OH groups, the surface roughness of the fiber increases, exposing more reactive sites and improving adhesion to the matrix, which significantly favors the mechanical behavior of the composite [7].

Average Pore Radius

Figure 2 shows the average pore radius of the pure PA6 membrane and its hybrids, which contain 0.33%, 1%, and 3% sisal fiber. The pores of the membranes are microscopic channels that allow the passage of substances and are essential in filtration and separation processes.

In the case of the PA6 membranes analyzed, the average pore radius of the pure and 0.33% sisal fiber membranes is smaller than that of the membranes containing 1% and 3% fiber. This behavior can be explained by the influence of the fiber concentration on pore formation, with a gradual increase in the average pore radius as a function of the increase in the percentage of fibers added to the polymer matrix.

When the fiber concentration is high, as in the case of the membranes with 3% fiber, pore dilation may

Figure 1. a) Water absorption and b) Porosity of pure PA6 membranes and hybrids with 0.33%, 1%, and 3% sisal fiber.

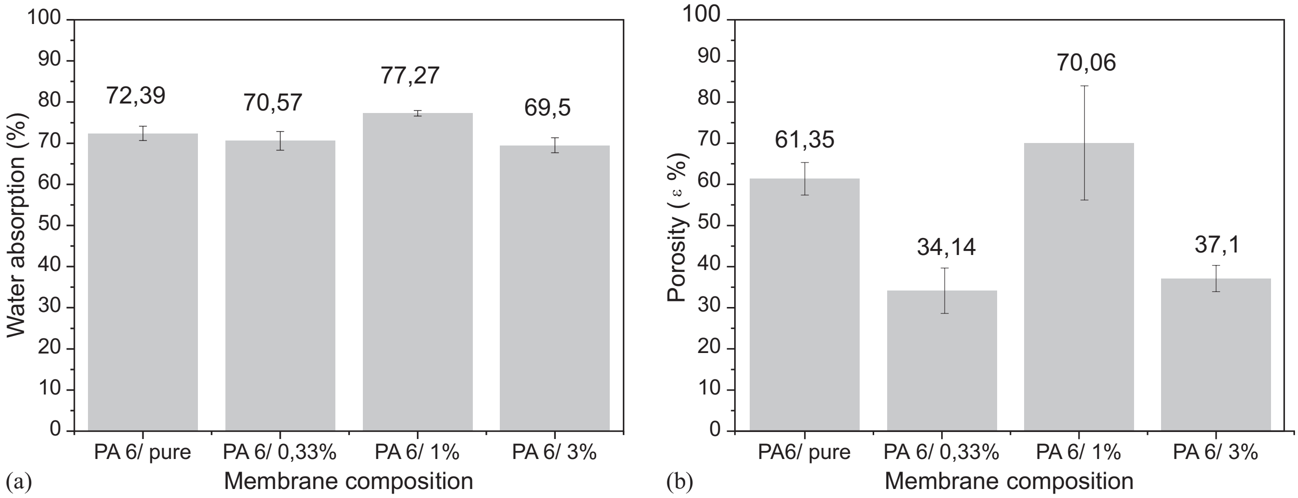
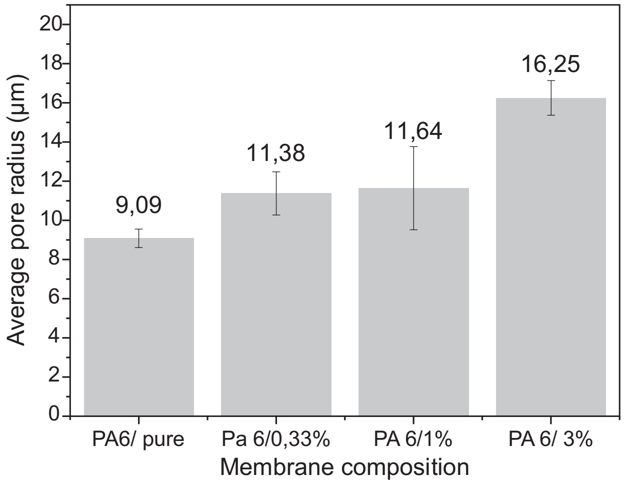


Figure 2. The average radius of the pure and hybrid PA6 membranes with 0.33, 1, and 3% sisal fiber.



occur, resulting in an increase in the average radius. On the other hand, a very low fiber concentration (0.33%) may also lead to pore dilation, possibly due to changes in the flow and temperature of the water during the membrane formation process. Therefore, the amount of fibers incorporated and the process conditions, such as the water temperature, affect the average pore radius.

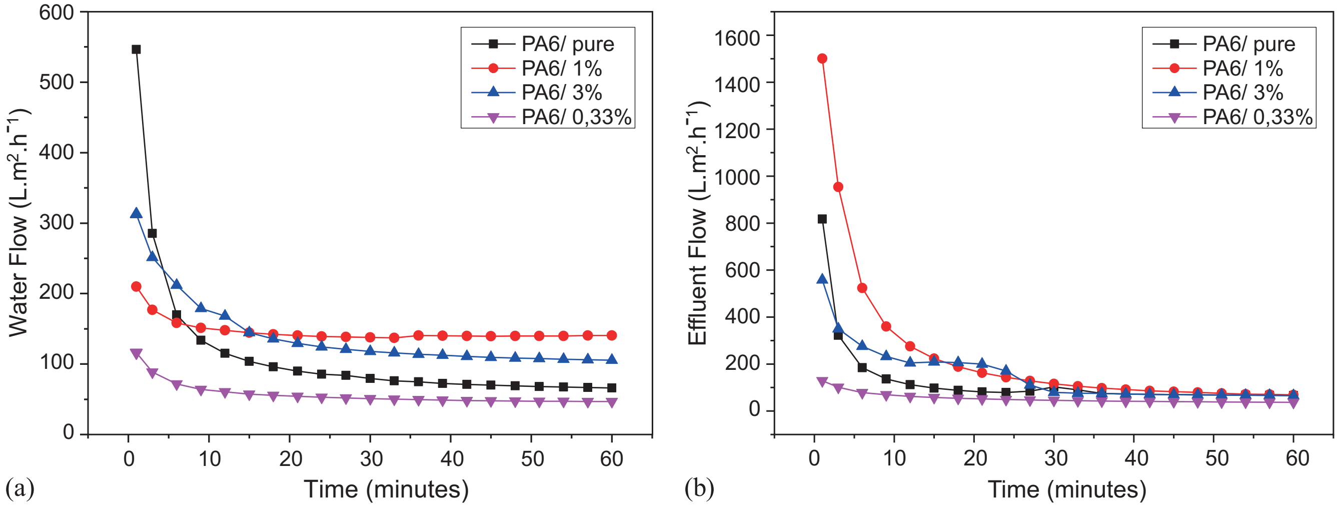
Flow Measurements

The curves presented in Figure 3 illustrate the flux measurements performed, providing a visual representation of the permeability characteristics of the membranes. Initially, a decrease in flux was observed in Figure (a), followed by a stabilization approximately 20 minutes after the start of the measurement. This stabilization can be attributed to a mechanical compaction process induced by the applied pressure or to the eventual swelling of the membranes since exposure to water tends to gradually reduce the size of the pores, directly influencing their permeability. The membrane with 0.33% sisal fiber presented the lowest flux, while the membrane with 1% fiber presented a slightly higher flux than the other membranes. This suggests that the fiber concentration influences the pore dilation.

Figure (b), with the addition of the dye, shows that, during the measurements, an initial decrease in flux occurred, followed by stabilization after approximately 25 minutes. The membrane containing 1% sisal fibers presented the highest initial flux, which subsequently stabilized. The membrane with 0.34% sisal fibers presented the lowest flux throughout the measurement period. These observations indicate that the amount of sisal fibers significantly affects the flux behavior and stabilization of the membranes. In general, we can observe that the permeate fluxes of both water and effluent occurred a gradual increase in fluxes with the increase in the concentration of sisal fiber added to the polymer matrix, following a behavior

Similar to that obtained for the average pore radius. In addition, it is possible to observe an increase in the values of the permeate fluxes with the effluents, probably due to the increase in the temperature of the effluents over time, which has dilated the pores of the membranes without compromising the separation performance of the membranes.

Figure 3. a) Water permeate flux of pure PA6 membranes and their hybrids with 0.33, 1, and 3% sisal fiber at 1.0 bar pressure. b) Permeate effluent flow with the addition of dye from pure PA6 membranes and their hybrids with 0.33, 1, and 3% sisal fiber at a pressure of 1.0 bar.



Membranes Yield

Dyes are highly pigmented organic compounds impart color to materials by selectively absorbing light [8]. By analyzing the concentration of the diluted dye in the effluent, we can determine the specific wavelength associated with the dye. In addition, this method allows us to evaluate the amount of dye remaining in the effluent after treatment. The visible light absorption range for dyes ranges from 428 to 512 nm. Using spectrophotometry, we identified the absorption peak of the dye and constructed an absorbance curve, as illustrated in Figure 4 (a), for concentrations of 50 mg.L^{-1}, 100 mg.L^{-1}, 200 mg.L^{-1}, 300 mg.L^{-1}, 400 mg.L^{-1}, and 500 mg.L^{-1}.

Using the calibration curve for dye absorbance at varying concentrations from 50 50 mg.L^{-1} to 500 50 mg.L^{-1}, we derived a linear fit equation ($y = 0.00129x + 0.01965$, where y represents the dye concentration based on absorbance) with a coefficient of determination (R^2) of 0.99774, as depicted in Figure 4(b). This result indicates that the absorbance for the dye at each concentration follows a linear relationship. With the calibration curve established, we can now determine the dye concentration in the permeate by correlating the wavelength with the absorbance reading.

Subsequently, we evaluated the membrane efficiency (%) (Table 1). All membranes tested in the dye separation process in water at a concentration of 500 mg.L^{-1} exhibited a significant dye reduction in the permeate, reaching efficiencies higher than 95%.

Figure 4. a) Absorption spectra of red dye at concentrations of 50 mg.L^{-1}, 100 mg.L^{-1}, 200 mg.L^{-1}, 300 mg.L^{-1}, 400 mg.L^{-1}, and 500 mg.L^{-1}. b) Dye absorbance calibration curve.

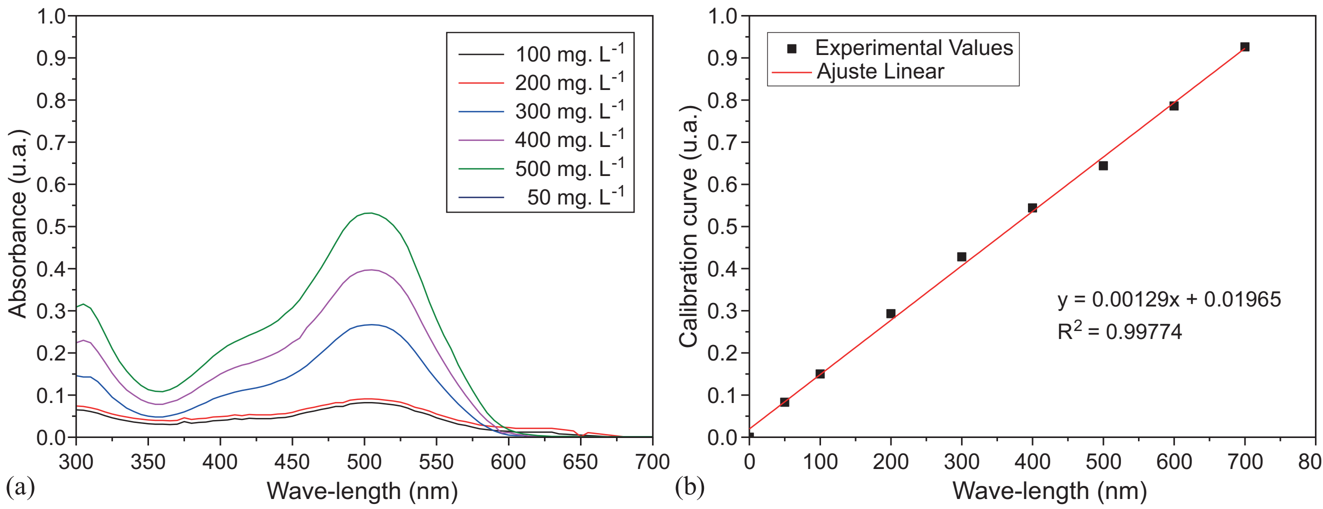


Table 1. The concentration of non-permeated dye at 500 mg.L^{-1} and yield.

Membrane Composition	Absorbance (ua)	Concentration (mg/L^{-1})	Yield (%)
PA6/Pure	0.161	8.28	98.34
PA6/0.33%	0.421	21.55	95.69
PA6/1%	0.019	1.04	99.79
PA6/3%	0.359	18.38	96.32

Conclusion

Hybrid membranes of polyamide 6 (PA6) reinforced with sisal fibers were successfully developed using immersion-precipitation. The study demonstrated that the fiber content significantly influences the porosity and retention capacity of the membranes. Specifically, water absorption decreased with higher fiber concentrations, indicating a strong correlation between fiber content and porosity.

The addition of sisal fibers enhanced the mean pore radius, improving the membranes' permeability characteristics. Flux measurements confirmed hybrid membranes exhibited superior permeate flux compared to pure PA6 membranes. Moreover, all membranes achieved a high dye separation efficiency, with yields exceeding 95%, confirming their potential application in microfiltration systems and the treatment of textile effluents.

This research highlights the viability of using renewable resources, such as sisal fibers, to improve polymer membrane performance, offering a sustainable alternative for advanced separation processes.

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