Circular Economy: Transforming Sericulture Waste into Biomaterials Through Electrospinning

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This study extracted silk sericin (SS) and silk fibroin (SF) from *Bombyx mori* cocoons to produce nanofibers through electrospinning. The membranes were made from polymeric solutions composed of SS, SF, PVDF, DMA, and TiO_2, aiming to electrospun water-stable membranes impregnated with metallic semiconductors. TiO_2 stands out from other catalysts due to its chemical properties and exemplary performance in photocatalytic contaminant removal compared to previous research [8]. With its chemical properties and exemplary performance in photocatalytic contaminant removal, it stands out from other catalysts. The impact of SS and SF on the membranes was analyzed, making it possible to conclude that SF increased the photocatalytic efficiency of the membrane by 17.89% during the tests. The innovative approach of incorporating fibroin in the membrane sparked intrigue and interest in the potential of this research.

Introduction

Sericulture is an ancient culture that integrates the cultivation of *Morus sp.* and the breeding of silkworms (Bombyx mori) [1]. Nowadays, Brazil is one of the great producers of green cocoons and is the country with the most significant production in Latin America.

B. mori cocoons comprise three protein components: silk fibroin, silk sericin, and P25. Fibroin is the main constituent of silk wire, representing about 70% to 80% of the total mass of the cocoons, while sericin (about 30% in mass) presents fundamental plastic properties to keep fibroin wires attached. P25 is a glycoprotein with an important rule on the integrity of the silk wire [2.3].

PVDF is a semicrystalline polymer with high mechanical resistance beyond thermal and chemical stability. It is hydrophobic and highly resistant to aging. This polymer is soluble in many organic solvents, such as DMA [4.5].

The electrospinning technique can produce fibers with tiny diameters on nanometric or micrometric scales. Due to its versatility, this technology has shown significant advantages over other methods in manufacturing nanofibers, as it enables control of the membrane's structure, porosity, orientation, and dimension [6].

The expression "emerging contaminants" refers to compounds that are not legislated and potentially harmful to human health. Those substances are not covered by traditional water treatment stations [7].

Previous research applied TiO_2 suspended in a contaminant solution to perform a photocatalysis process, which can produce a substantial amount of sludge, necessitating many filtration steps [8]. Even in electrospinning, the catalysts are usually impregnated after a previous process to make the membrane, like the one reported by AZNAR-CERVANTES et al. [9]. This research, however, aims to produce membranes used in photocatalysis from proteins extracted from B. mori cocoons and add the catalysts directly into the polymeric solution. This approach could solve the main problem of TiO_2 use in photocatalysis, making the process more efficient and less wasteful.

Materials and Methods

The cocoons were first degummed in an autoclave at 100°C for 1 hour to extract sericin and cooled at room temperature. Then sericin, now in solution, was filtered from the remaining cocoons and frozen at -4°C for 24 hours to fractionate the protein. After achieving room temperature, the high molar mass sericin created a superficial gel on the filtrated solution and stored it in the freezer.

The fibroin extraction process began with degumming, using a calcium carbonate solution 20nM and boiling it for 30 minutes. The remaining cocoons were washed with ultrapure water and dried at 25°C. The cocoons were then added to a ternary solution made of calcium chloride, methanol, and water to solubilize fibroin.

A 15% PVDF/DMA solution was made under agitation and heating. After that, three samples of the solution were used to prepare distinct polymeric solutions: 10% sericin (I), 10% fibroin (II), and the 15% PVDF/DMA (III). TiO_2 was added to the solutions at a 0.23% concentration, still under agitation and heating. The electrospinning of the solutions operated at a flow rate of 0,53 mL/h, using a voltage of 18 kV and 10 cm work distance. So, after it was done, the resulting membranes were submitted to a solubility test.

After the membranes were electrospun, the photocatalysis tests were done in an artificial irradiation module, using 16 cm^2 of each membrane fixed on individual beakers containing 100 mL of methylene blue (MB) 10 $mg.L^{-1}$ at pH 7. The solution parameters were determined based on IMAMURA et al. [8], aiming to simulate the best conditions of the photocatalysis process. The dye concentration was measured by spectrophotometry using a calibration curve with samples withdrawn at 5, 10, or 30 intervals.

Results and Discussion

The membrane with 15% PVDF/DMA showed good fiber formation, homogeneity, and a diameter of 15.5 cm. It also behaved as insoluble in water.

Adding sericin, fibroin, and titanium dioxide to the solution appropriately formed and remained homogeneous, emphasizing the membrane containing fibroin. For the solubility test, the membrane's mass was evaluated before and after 20 hours under agitation, and its variation is inserted in Table 1, where the blank is PVDF/DMA/TiO_2.

Table 1. Results of the membrane solubility test

Membrane	Initial mass (g)	Final mass (g)	Mass variation (%)
Blank	0,0225	0,0223	0,0089
Fibroin	0,0171	0,0163	0,0468
Sericin	0,0147	0,0142	0,0340

Therefore, it can be concluded that the membranes lost no significant mass within 20 hours in water, not exceeding 0.1% of lost mass. The absorbance test in the supernatant water showed no apparent change, indicating no evident leaching. These successful solubility test results provide reassurance and confidence in the research.

An analytical curve was first constructed to calculate photocatalytic efficiency, enabling concentration calculation from absorbance and removal. IMAMURA *et al.* [8] found the optimal conditions for using suspended TiO_2 (500 ppm) as a photocatalyst in the degradation of MB at pH 7.00. After 180 min, the photocatalytic efficiency was 94.82%, forming the basis for the photocatalytic tests with the membranes. However, the disadvantage of using suspended TiO_2 is the sludge formed at the end of the process. Thus, in this study, TiO_2 was incorporated (250 ppm in the polymeric solution) in an electrospun fiber using PVDF as the polymer and Sericin and Fibroin as copolymers. For each membrane synthesized, the data is compiled into a graph of efficiency in methylene blue degradation over time (Figure 1).

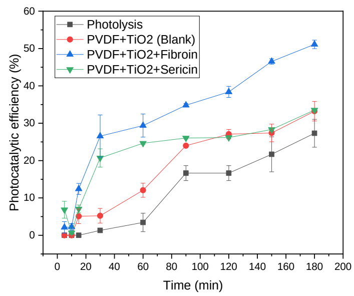

Figure 1. The photocatalytic efficiency of membranes in the degradation of MB as a function of reaction time under UV light, conducted at pH 7.00.).

By analyzing Figure 1, the membrane containing fibroin exhibited the highest degradation, reaching 51.12% degradation of methylene blue, indicating that fibroin contributed to greater efficiency, as the blank with catalyst removed only 33.22%. Therefore, being a catalytic reaction, it can be affirmed that the presence of fibroin in the membrane enables more significant contact between the contaminant solution and the catalyst, potentially acting as a pore-forming agent. Thus, adding fibroin to the membrane resulted in a 17.89% improvement in removal. As a result, using TiO_2 incorporated in the electrospun membrane in a one-pot process solved the problems of its reuse in mild operating conditions. Finally, it is possible to infer that this research achieved its goals and contributed significantly to developing and optimizing this type of technology.

Conclusions

The main problem of using TiO_2 in photocatalysis was solved by incorporating proteins extracted from the *B. Mori* cocoon into the production of electrospun membranes, obtaining stable and satisfactorily homogeneous membranes. Also, the proteins promoted a significant increase in process efficiency compared to the membrane (I), with fibroin membrane (II) removing 51.12% of the contaminant.

Acknowledgments

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References

[1] SANTOS, V. C., SOUZA, K.A, *et al*., in *Informativo técnico do Semirárido*, volume 10 (2016) page 62.
[2] DASH, R., MANDAL, B. B., KUNDU, S. C., in *Journal of Biotechnology*, volume 144 (2009) page 321.
[3] Yu-Qing Zhang., in *biotechnology advances*, volume 20 (2002) page 91.
[4] Fu Liu, N. Awanis Hashim, *et al.*, in *Journal of membrane science*, volume 375 (2011) page 1.
[5] Guo-dong Kang, Yi-ming Cao, in *Journal of Membrane Science*, volume 463 (2014) page 145.
[6] Avinash Baji, Yiu-Wing Mai, *et al.*, in *Composites Science and Technology*, volume 70 (2010) page 703.
[7] TORDIN, Cristina, "Contaminantes emergentes podem ser uma ameaça na água para consumo humano" in *Embrapa* (2018).
[8] IMAMURA, N. M.; ZACARIAS, L. R. Z.; GIMENES, M. L.; MARTINS, D. C. C. Aplicação em fotocatálise heterogênea na degradação do azul de metileno in *Encontro Internacional de Produção Científica da UniCesumar* (2023).
[9] Salvador Aznar Cervantes *et al., The Royal Society of Chemistry ,* v.10 (2020) page 1917.