ORAL/POSTER
Ph.D. Student: Y/N
Journal: NONE

Incorporation of Polydopamine and TiO_2 in PVDF Membrane for photocatalytic effect in oil/water separation

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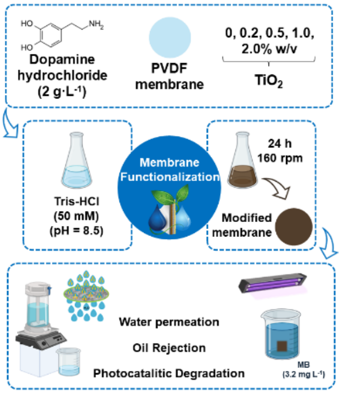

This study demonstrates a facile method for modifying the surface of poly(vinylidene fluoride) (PVDF) membrane with polydopamine and TiO_2 to increase water permeation in the oil/water separation process and impart photocatalytic capacity to the membrane. A commercial PVDF membrane was modified with TiO_2 concentrations ranging from 0.2 to 2.0% by weight and 2 g L^{-1} polydopamine. Membranes modified with 1.0% TiO_2 presented greater water permeability and photocatalytic capacity without significantly interfering in the oil rejection compared to the neat membrane and other modification conditions. Results demonstrate the great capacity of TiO_2/PDA for simultaneous separation and degradation.

Introduction

The improper disposal of industrial effluents containing oily compounds is an environmental issue of great concern. Given the potential toxic substances, such compounds directly threaten the environment and human health [1].
Processes using membranes appear to be a promising alternative to conventional industrial effluent treatment methods. Although many applications have been developed, improving the separation performance, fouling resistance, and stability of membranes remains challenging [2].
Photocatalytic processes emerge as a promising solution to overcome some of these limitations. However, the efficient incorporation of the catalyst into the membrane requires more specific studies, given the variety of methods available, each with its advantages and disadvantages [3].
Modifying the membrane surface is one of the ways to incorporate different materials into its matrix. In recent years, the use of polydopamine (PDA) as a binding agent between the membrane and the modifying material has gained prominence. TiO_2 is a versatile, cheap, stable, and abundant compound widely described in the literature as having great photocatalytic capacity and hydrophilic nature. It is ideal for modifying membranes used in oil/water separation [4].
This study investigates and demonstrates a practical method of polymeric membrane modification using PDA and TiO_2 to improve the membrane hydrophilicity and evaluate its oil rejection and photocatalytic capacity.

Material and Methods

Initially, a solution of dopamine hydrochloride in Tris-HCl buffer solution (pH 8.5, 50 mM) was prepared and added to a 125 mL Erlenmeyer flask, followed by the addition of TiO_2 to this solution and homogenization. The PVDF membrane previously prepared and cut into discs (5 cm) was then added to the Erlenmeyer flask, immersed in the solution, and placed on an orbital shaker for 24 hours at 30°C. After completing the reaction time, the membrane was rinsed with ultrapure water to remove excess solution that did not adhere to the surface, dried in an oven at 65 °C for 24 hours, and stored.
The membrane modification process was carried out using a concentration of 2.0 g L^{-1} of dopamine hydrochloride and TiO_2 ranging from 0.2 to 2.0% (w/v) while maintaining the medium agitation at 160 rpm. The membrane permeation performance was evaluated against a standard soybean oil emulsion (1.0 g L^{-1}), and their photocatalytic capacity was evaluated against the degradation of methylene blue (MB) (3.2 mg L^{-1}). Oil quantification was based on total organic carbon (TOC), and MB concentration was determined using a UV-vis spectrophotometer at a wavelength of 665 nm.

Results and Discussion

The results obtained for water permeance, and oil rejection are presented in Figure 1. We can observe that PDA deposition caused a decrease in the flux of the PVDF membrane from 462 to 191 kg h^{-1} bar^{-1} m^{-2}, probably due to partial obstruction of the pores by the biopolymer. Adding up to 1% TiO_2 to the coating solution caused an increase in permeance. A 2.3-fold increase in water flow was obtained by incorporating 1.0% TiO_2. Further increasing this value to 2.0% caused a reduction in permeance to 781 kg h^{-1} bar^{-1} m^{-2}, indicating that a higher concentration of titania was ineffective and likely contributed to pore blockage. Proner et al. [5] have previously reported a decrease in permeance with the PDA deposition process. Strategies that seek to recover this characteristic are of paramount importance, and the application of TiO_2 shows promising results, indicating that the applied process is effective in recovering water flux.

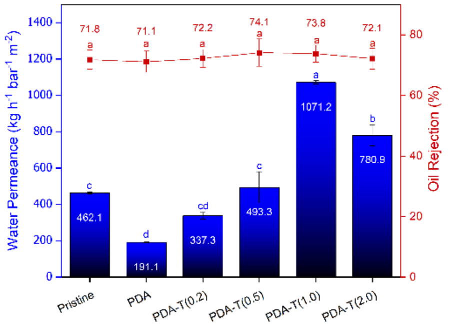

Figure 1. Water permeation and oil rejection of membranes modified with PDA and TiO_2 at different concentrations.

No significant difference was observed between the membranes evaluated regarding oil rejection, indicating that the modification did not affect oil removal, even with the greater permeate flux obtained. It is worth mentioning that the values presented refer to the TOC of the oil and surfactant (SDS) used in the emulsion, with the presence of SDS representing approximately 24.7% of the emulsion total TOC.

Figure 2 shows the results obtained for the MB degradation of each membrane. It is possible to observe that the degradation behavior was like that observed for water permeance, which indicates that it was indeed TiO_2 that was incorporated into the membrane since this component has photocatalytic capacity. The pure and with PDA membranes showed low degradation, which was not statistically different from the photolysis process, indicating that the MB reduction resulted only from the action of UV light. It is observed that even with a low concentration of TiO_2 (0.2%), the membrane managed to degrade around 59% of the contaminant. In the best condition, 1.0% TiO_2, the degradation was close to 89%, indicating that the PDA/TiO_2 modification effectively obtained a photocatalytic membrane.

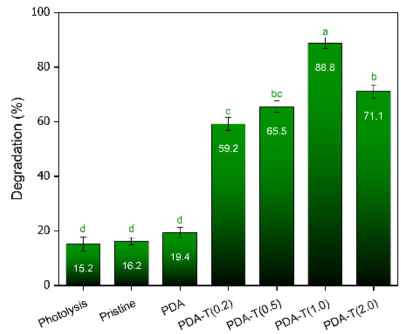

Figure 2. MB degradation of membranes modified with PDA and TiO_2 at different concentrations.

Conclusions

The membrane modified with 1.0% TiO_2 showed the best water permeance and photocatalytic performance. The results indicate that incorporating TiO_2 gave a better hydrophilic character to the membrane surface and did not interfere with oil rejection. Furthermore, the membrane presented greater photocatalytic capacity, demonstrating the possibility of being used simultaneously for separation and degradation.

Acknowledgments

The authors acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support.

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