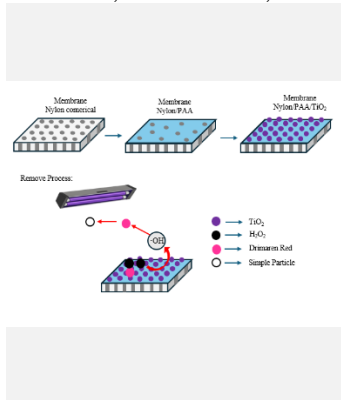


DEVELOPMENT OF A HYBRID MSP-AOP PROCESS THROUGH MEMBRANES IMPREGNATED WITH TiO₂ NANOPARTICLES

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Emerging contaminants (EC) pose a significant challenge in water treatment because of their resistance to conventional methods. To address that, a novel approach integrating Membrane Separation Processes (MSP) with Advanced Oxidation Processes (AOP) has been developed. This approach combines the advantages of each process while mitigating their respective limitations and offers a promising solution for EC removal. In this study, TiO₂ nanoparticles were impregnated into nylon polymeric membranes using the chelating agent polyacrylic acid. The performance of the combined process was analyzed using Drimaren red dye in a recirculation flow system. The nylon membrane with TiO₂ nanoparticles coupled with UV radiation achieved a dye removal efficiency of 85%. Furthermore, the influence of the H₂O₂ concentration was investigated, revealing an optimal concentration of 10 mM. By achieving significant removal rates, the MSP-AOP hybrid process presents a promising innovation for wastewater treatment.

Introduction

Emerging contaminants (EC) are compounds found in different water bodies that are difficult to degrade and can cause serious public health problems, such as pharmaceuticals, dyes, and pesticides [1]. Conventional treatments are ineffective in removing these substances; however, techniques such as Advanced Oxidative Processes (AOP) and Membrane Separation Processes (MSP) can remedy this problem.

AOP can generate hydroxyl radicals ($\cdot\text{OH}$), a species that allows the degradation of EC [2]. There are different forms of AOP, including Fenton, Photo-Fenton, and Heterogeneous Photocatalysis, which vary in reagents and operating conditions.

Heterogeneous Photocatalysis, specifically with TiO₂, has attracted attention because of its high efficiency in removing organic matter and low waste generation [3]. Nanoparticles of this dioxide have several attractive characteristics such as high photocatalytic activity and production capacity under environmental conditions [4]. However, they clump together and form larger particles, creating problems separating them from treated water [5]. One way to solve this problem is to immobilize it on a support. Polymeric membranes, such as nylon membranes, can support nanoparticles during AOP. In addition to being inert, they are frequently used in the treatment of effluents [6,7,8]. An advantage of combining the two processes is that AOP can act synergistically with MSP, reducing the fouling of organic matter on the membrane surface [7,9]. Therefore, it would be interesting to develop a hybrid MSP-AOP process to improve the EC degradation efficiency.

The present study aimed to investigate the MSP-AOP hybrid process by removing a model contaminant, Drimaren red dye (DR), using a nylon

membrane functionalized with TiO₂ nanoparticles.

Material and Methods

A commercial nylon membrane (Whatman, 0.45 μm) was functionalized with TiO₂. To improve the loading, a chelating agent was added to the membrane pores via polymerization with polyacrylic acid (PAA) using the microwave technique described by Silva et al. [6]. Nanoparticle impregnation was achieved by immersing the modified membrane in a solution under ultrasound [9].

Quantification of DR contaminant was performed using spectrophotometry (517 nm). The experiment was conducted in a permeation setup containing a UV chamber (254 nm) coupled to the membrane cell, recirculating the retentate and the permeate. The initial process conditions were $[\text{H}_2\text{O}_2]=10\text{mM}$, $[\text{DR}]=5.0\text{mg/L}$, $P=1.0$ bar and $\text{pH}=4.5$ with pH adjustment to the initial value during the experiment. The permeate current was analyzed at defined time intervals to observe the reduction in pollutant concentration.

Results and Discussion

First, experiments for DR removal were carried out using a commercial nylon membrane, a nylon membrane with PAA, and a membrane with TiO₂ nanoparticles. The experiment with the unmodified nylon membrane yielded a permeate with approximately 25% dye removal (Figure 1). The addition of the chelating agent, nylon/PAA membrane, allowed the removal to be approximately 15% higher than that of the neat membrane. Better removal was obtained with the membrane impregnated with TiO₂ under UV light, which allowed a permeate stream with only 15% of the initial concentration of the pollutant model.

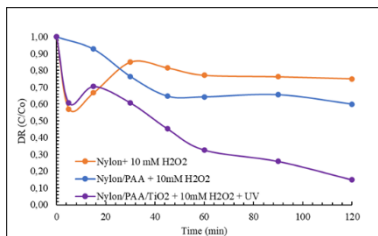


Figure 1. Removal of Drimaren red dye by Nylon, Nylon/PAA, and Nylon/PAA/TiO₂ membranes.

The hydrogen peroxide concentration is an important parameter in photocatalysis experiments, as it can act as a radical scavenger [2]. To determine this influence, tests were carried out on a membrane loaded with TiO₂ nanoparticles using three different concentrations of H₂O₂ (Figure 2). At the lowest concentration, 5mM, was approximately 38% of the

initial pollutant concentration in the permeate, whereas at the highest concentration (15 mM), only 11% of the dye was present in the permeate. Similar dye removal was observed in the test with 10 mM H₂O₂.

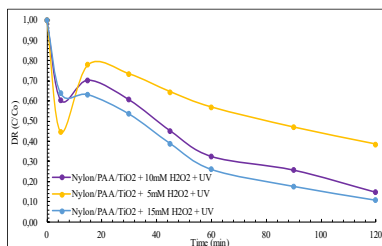


Figure 2. Removal of Drimaren Red dye with the Nylon/PAA/TiO₂ membrane with different concentrations of H₂O₂.

Conclusions

The MSP-AOP hybrid process is a new approach for removing micropollutants that overcomes the challenges faced by individual techniques.

The commercial nylon membrane removed approximately 25% of the dye, while the functionalized membrane (Nylon/PAA/TiO₂) removed 85% of the initial dye. When comparing different concentrations of H₂O₂, it is possible to note that the ideal concentration is 10 mM, as it obtained the best result when comparing removal and reagent expenditure.

Nylon membranes impregnated with TiO₂ nanoparticles under UV radiation combine MSP-AOP in only one step and are effective for emergent contaminant removal processes.

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