**DEVELOPMENT OF NYLON MEMBRANES FUNCTIONALIZED WITH ZERO-VALENCE IRON NANOPARTICLES FOR THE REMOVAL OF ORGANIC CONTAMINANTS**

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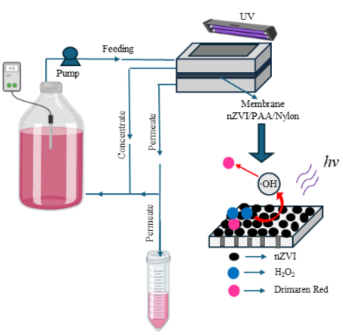


The Fenton Process is an important treatment for the degradation of organic contaminants in wastewater. However, inherent limitations promote the investigation of new approaches. In this context, zero-valent iron nanoparticles (nZVI) are a promising alternative, but their agglomeration causes a loss of process efficiency. To solve that, the particles were immobilized on nylon membrane, generating a hybrid MSP-AOP process. The presence of nZVI in the membrane was confirmed by EDS analysis, in addition to being observed by the characteristic peaks in FTIR and increased hydrophilicity compared with the commercial membrane The treatment of organic compounds was investigated using the Drimaren Red dye. UV radiation was shown to improve the dye removal by 13% more than the process without UV. Therefore, the MSP-AOP hybrid process, which consists of a nylon membrane with nZVI, is a potential innovation for effluent treatment.

## Introduction

Advanced Oxidative Processes (AOP) and Membrane Separation Processes (MSP) are essential for the treatment of organic contaminants such as dyes and emerging contaminants in water and wastewater.

The Fenton Process is an example of an AOP that involves the reaction of iron ions with hydrogen peroxide under mild temperature and pressure conditions [1,2]. The simplicity of the operation, in addition to the possibility of treating various contaminants, highlights this process. Despite these advantages, this process has some limitations including sludge formation, continuous iron loss, and acidic pH [2,3].

To overcome such difficulties, a Heterogeneous Fenton Process has been developed, which uses a solid substrate to generate hydroxyl radicals, the main compounds in the AOP. Among these catalysts, zero iron nanoparticles (nZVI) are considered environmentally friendly and have a high removal of organic contaminants. Furthermore, this process reduces iron leaching, resulting in lower reagent consumption and no sludge formation [2,3,4].

Although nZVI exhibits excellent qualities owing to its size and magnetic properties, agglomeration is a major challenge [5]. One way to overcome this problem is to explore the immobilization of nZVI particles by adsorbing them onto a surface, thereby allowing a more significant number of free active sites.

Polymeric membranes, such as nylon, are excellent materials for use as supports because they are inert, inexpensive, and can be used in the treatment of water and effluents [6]. On the other hand, the nZVI loaded in the membranes can improve their performance owing to reduced fouling, and consequently, improve the useful life of the membrane [4,5].

The development of a hybrid MSP/AOP process can minimize the advantages of both methods and improve their performance.

Therefore, this study aimed to develop and characterize a nylon membrane impregnated with zero-valent iron nanoparticles, in addition to investigating its organic compound removal effect.

## Material and Methods

A commercial nylon membrane (Whatman 0.45 μm) was used to load the nZVI nanoparticles. To increase the nanoparticle layer on the surface, the chelating agent polyacrylic acid (PAA) was added and PAA polymerization was performed using a microwave technique [4]. The nanoparticles were impregnated in situ, according to the methodology described by Silva et al. [4]. The membranes were characterized by contact angle measurements, Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

The performance of the MSP/AOP hybrid was evaluated using the dye Drimaren Red (DR) as a model contaminant in pollutant removal tests in a crossflow membrane system. The MSP/AOP system was operated at pH 4.5 (maintained throughout the experiment), with $[H_2O_2]_0$= 10 mM, $[VDR]_0$= 5 mg/L, and P= 1 bar, and recirculation of the retentate and permeate. In addition, the membrane cell allows UV-254 nm radiation of the surface through a quartz plate. During the experiments, aliquots were removed from the permeate at specific times to analyze the DR concentration and permeate flux.

The DR quantification was performed using a spectrophotometer at a wavelength of 517 nm.

## Results and Discussion

Contact angle analysis demonstrates the hydrophilicity of the membrane. Three membranes were tested: a commercial nylon membrane, a commercial membrane (Nylon) with PAA (Nylon/PAA), and a membrane functionalized with nanoparticles (Nylon/PAA/nZVI) (Figure 1). The addition of PAA increased the hydrophilicity of the membrane, as evidenced by the reduction in the contact angle compared to the commercial membrane (56.8° to 39.7°), which was due to the presence of carboxylic groups, as determined by FTIR analysis (Figure 2). The nylon/PAA/nZVI membrane achieved the highest hydrophilicity among the three membranes, with a contact angle of 28.3°, owing to the presence of nanoparticles.

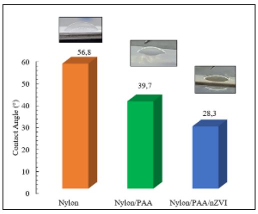


**Figure 1.** Contact angle of commercial nylon membranes (Nylon), with the chelating agent polyacrylic acid (Nylon/PAA) and with the addition of the nZVI (Nylon/PAA/nZVI).

The photomicrographs showed that PAA was mainly responsible for the reduction in pore size when comparing the nylon/PAA/nZVI membrane with Nylon and Nylon/PAA membranes. Furthermore, coupled EDS analysis confirmed the presence of iron in the functionalized membrane, which can also be seen in FTIR by the disappearance of the peak corresponding to the carboxylic group, which would be linked to the nanoparticle.

The efficiency of the membrane separation process without oxidative process was analyzed by testing a commercial nylon membrane. This membrane removed approximately 23% of the dye from the permeate after 1h of the experiment, with a final flow rate of 772.02 L/h•m$^2$. In contrast, the hybrid process (Nylon/PAA/nZVI membrane) achieved a 30% reduction in permeate concentration after 1 h, with a final permeate flow rate of 2300.83 L/h•m$^2$, 3 times greater than that of the membrane process. Therefore, the presence of nanoparticles is advantageous for treating model contaminants.

The presence of ultraviolet radiation can impact the process, given the occurrence of the photo-Fenton process; therefore, the test was also carried out in the presence of UV light [1]. In this case, the process achieved the highest removal rate (43%), indicating that the photocatalytic process resulted in significant generation of radicals.

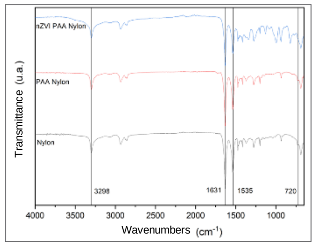


**Figure 2.** FTIR analysis of commercial nylon membranes (Nylon), with the chelating agent polyacrylic acid (Nylon/PAA) and with the addition of the nZVI (Nylon/PAA/nZVI).

## Conclusions

The MSP/AOP hybrid process is an innovative approach for effluent treatment. To understand this process, nZVI-loaded nylon membranes were studied. The presence of the chelating agent and nZVI increased the hydrophilicity of the membrane. Regarding the pollutant removal tests, the nylon membrane removed 23% of the dye, while the nylon/PAA/nZVI membrane removed 7% more dye, in addition to a permeate flux three times higher. When analyzing the results in the presence of UV radiation, it was clear that UV radiation could remove a significant portion of the dye in 1h (43%).

Therefore, the functionalized membrane developed in this study is a potential alternative treatment that should be further explored as it demonstrates a synergistic effect between the techniques.


***Acknowledgments***

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