# Modified Photocatalytic Membranes Applied to the Treatment of Petroleum Refinery Effluent

ORAL
Ph.D. Student: N
Journal: JECE

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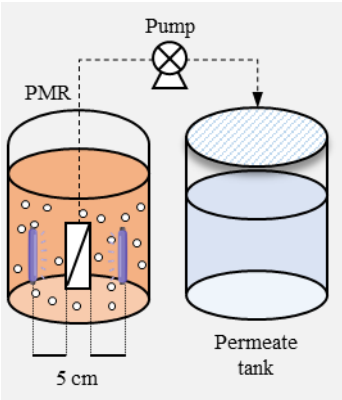


This study evaluated membranes modified with dopamine and GO-$TiO_2$ in a photocatalytic membrane reactor (PMR) for treating oil refinery wastewater. Photocatalytic activity was activated with a distance of 5 cm between the light source and the membrane, resulting in better fouling control compared to UV light turned off. After 24 hours of irradiation of a membrane subjected to adsorption, there was degradation of the adsorbed organic compounds and a 71% increase in permeability. This suggests that UV light can selectively activate photocatalytic activity and assist in cleaning the membrane and recovering permeate flux. Modified membranes show promise in treating wastewaters from the petrochemical industry, but more studies are needed to understand their interaction with the effluent under UV light.

## Introduction

Activities in refineries and petrochemical plants involve various processes that are sources of wastewaters generation, which typically contain oil and grease, aromatic hydrocarbons, solids and toxic metals that can cause environmental and human health disturbances if discharged without proper treatment [1]. Therefore, it is essential to employ effective treatment techniques to reduce environmental damage and enhance process sustainability. Although membrane technologies have shown unique benefits in this context, including high contaminant rejection and the possibility of reusing permeate, their application is limited by fouling phenomenon, which reduces membrane lifespan and selectivity over time [2]. Current literature suggests that surface modifications of membranes with photochemical-capable oxides can mitigate this phenomenon [3]. It is important to note that at the end of their lifespan, membrane modules are usually discarded in landfills, and recycling membranes is a way to extend their durability and reduce environmental damage from their disposal [4]. Thus, this study aims to evaluate the performance of a photocatalytic reactor with recycled end-of-life membranes modified with dopamine and graphene oxide and titanium dioxide nanoparticles (GO-$TiO_2$) nanocomposites applied to treat real refinery wastewater.

## Material and Methods

Reverse osmosis membranes at the end of their lifespan were recycled using a NaClO solution with a contact intensity of 300,000 ppm $h^{-1}$. Subsequently, the surfaces of the recycled membranes were coated with a layer of dopamine prepared in a basic medium and GO-$TiO_2$. Details of the membrane coating methodology can be found in our previous study [5]. The wastewater was collected at an oil refinery located in Minas Gerais, after secondary treatment with biodiscs. To verify the adsorption of organic compounds and photocatalytic activity, the membranes were submerged in the effluent for 15 weeks. Concurrently, the membranes were inserted in a photocatalytic reactor with aeration and UV lamps IP7 UV-C-Desinfection of 11 W power to observe permeate flow and anti-fouling capacity (pressure = 0.88 ± 0.02 bar, temperature = 23 ± 1 °C). The distance between the UV lamps and the membranes varied between 10 cm and 5 cm.

## Results and Discussion

A modified membrane (hydraulic permeability = 20.44 L $m^{-2}$ $h^{-1}$ $bar^{-1}$, membrane hydraulic resistance (Rm) = $1.98\times10^{12}$ $m^{-1}$) remained in contact with the effluent for 15 weeks. The adsorption effect of compounds present in the feed caused a 55% decrease in permeability in the modified membrane and an increase in resistance of over 2 times, with a value of $4.39\times10^{12}$ $m^{-1}$ after 15 weeks. Then, the membrane was irradiated with UV light for 24 hours at a distance of 5 cm between the light source and the membrane surface, resulting in a 71% increase in hydraulic permeability and a 41% decrease in the resistance of the fouled membrane. It is important to highlight that no degradation of the modified membrane surface was observed, as examined under an optical microscope at a 100-fold

magnification. This result indicates the activation of the photocatalytic process induced by UV light irradiation, contributing to the degradation of compounds adsorbed by the membrane without damaging the modified surface. The result also suggests that periodic activation of UV light could function as a membrane cleaning method, aiming to recover permeate flow. FTIR analysis showed that several transmittance bands were significantly reduced after UV light application, indicating the removal of pollutant compounds adsorbed on the membrane surface by photocatalytic activity assisted by $TiO_2$.

With the photocatalytic reactor, it was possible to verify that at a distance of 10 cm (Figure 1a) between the lamps and the membrane surface, there is no significant interference in permeate flow compared to the initial flow with UV light activation (p-value = 0.783). However, with the reduction of the distance between the UV lamps to 5 cm (Figure 1b), a significant delay in the decrease of normalized flow was observed (p-value = $4.0\times10^{-12}$), indicating a positive influence of membrane surface photocatalysis on permeate flow. This result indicates that the addition of the $TiO_2$ catalyst to the membrane, in the presence of UV light, can help control membrane fouling by degrading compounds that may have been deposited or adsorbed on the membrane surface, as observed in previous studies [6]. However, a removal of COD of 12% from the wastewater was observed in the condition of the deactivated UV lamp and only 2% in the condition of the activated UV light.

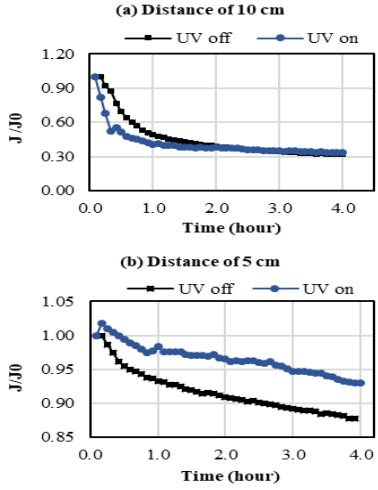


**Figure 1.** Flux over initial flux (J/J0) by the photocatalytic membrane modified with dopamine and GO-$TiO_2$ (a) with a distance of 10 cm between the UV lamps and the membrane (Rm = $1.5\times10^{13}$ $m^{-1}$) and (b) with a distance of 5 cm between the UV lamps and the membrane (Rm = $4.5\times10^{12}$ $m^{-1}$).

## Conclusions

This study evaluated recycled membranes modified with dopamine and GO-$TiO_2$ in a photocatalytic reactor for treating petroleum refinery wastewater. Photocatalytic activity was activated with a 5 cm distance between the light source and the membrane surface, resulting in improvements in fouling control compared to deactivated UV light. Additionally, after 24 hours of irradiation on a fouled modified membrane, there was degradation of adsorbed organic compounds and a 71% increase in permeability. This suggests that UV light can be applied selectively to activate photocatalytic activity and aid in membrane cleaning and permeate flux recovery. Thus, it is concluded that modified membranes can be effective in treating petrochemical industry wastewaters, but further studies are needed to understand their interaction with the effluent under UV light.

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