

PVDF-MIL-88A photocatalytic membrane to treat organic textile contaminant

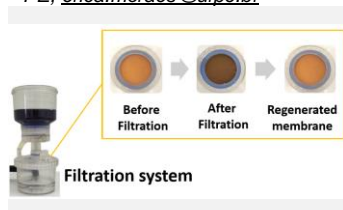
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The MIL-88A MOF was used to prepare photocatalytic membranes over PVDF support to treat textile effluent. MIL-88A structure was confirmed by XRD and FTIR characterization. The photo-Fenton reaction was the most efficient process for degradation of the organic contaminant to regenerate the membrane, obtaining with 100 % of degradation in 25 min reaction. The optimized membrane achieved high recyclability with an efficiency of 87.2 % of rejection rate and 82 L h⁻¹ m⁻² bar⁻¹ of permeation flux, after 13 cycles.

Introduction

Water plays an important role in industrial processes and services sector. However, rapid population growth, intense industrialization, and economic expansion have led to the daily discharge of a significant volume of untreated wastewater into the environment [1,2]. The textile industry consumes approximately 10000 tons of synthetic dyes per year, resulting in the production of around 100 tons of contaminated effluents [3].

Advanced Oxidative Processes (AOPs), which generally utilize the hydroxyl radical (HO[•]) for pollutant oxidation, have been applied in many types of effluent [4]. Among these AOPs, the Fenton reaction and photo-Fenton have received special attention. Membrane filtration technologies, such as microfiltration [5], is widely studied in separation processes and effluent treatment. However, there are limitations, such as the need for periodic backwashing to remove impurities retained in the membranes [6].

Considering the limitations of using membranes or Advanced Oxidative Processes (AOPs) alone, a promising strategy to treat effluents is the use of combined treatment processes. Photocatalytic membranes, modified by incorporating catalysts, have the ability to remove contaminants from aqueous media and promote their in situ degradation through photocatalytic reactions [7]. This work proposes the use of a photocatalytic membrane in a PVDF matrix with MIL-88A-type Metal-Organic Framework (MOF) for the treatment of a textile dye in aqueous.

Material and Methods

Synthesis of the MIL-88A MOF: The MIL-88A was synthesized via hydrothermal method. Iron(III) chloride (5 mmol, 8.112 g) and fumaric acid (5 mmol, 3.48 g) were dissolved in 180 mL of deionized water. For complete homogenization, the system was placed on a magnetic stirrer at 80 rpm and 70°C for 10 minutes. The solution was then transferred to a Teflon-coated stainless steel reactor and kept in an oven at 70°C for 12 hours. The precipitate was

centrifuged, washed three times with deionized water, and dried at 60°C for 10 hours [8]. Finally, MIL-88A was characterized by X-ray diffractometry and FTIR spectroscopy.

Membrane preparation: The MIL-88A obtained was used to prepare a suspension at a dosage of 40 mg of MIL-88A in 40 mL of deionized water. The mixture was vigorously stirred for 30 min. Subsequently, the suspension was sonicated for 15 min. The method of depositing MIL-88A on PVDF filters (4.7 cm diameter, 0.22 μm pore size) was accomplished through vacuum filtration of the MIL-88A suspension on the PVDF filter. The resulting membrane was named PVDF/MIL-88A.

Membrane evaluation: First, the ability of MIL-88A supported on the membrane to degrade RB5 dye (10 mg L⁻¹, 100 mL) by different processes was evaluated: photolysis, adsorption, heterogeneous photocatalysis, Fenton and Photo-Fenton. Given the best result, the recyclability of the membrane was evaluated by filtration-regeneration using measuring the permeation flux (1) and rejection (2) to RB5.

$$J = V / (A \cdot \Delta P \cdot \Delta t) \quad (1)$$

V (L) is the volume of the solution; A (m²) is the surface area of the membrane; ΔP is the pressure difference (bar) and Δt is the filtration time (h).

$$R = ((1 - C_f / C_0) \cdot 100) \% \quad (2)$$

R is the dye rejection rate; C_f is the concentration of the filtrate; C₀ is the concentration of the initial dye solution. The determination of RB5 concentrations before and after filtration was carried out using UV-VIS spectroscopy.

Results and Discussion

The characterization results are shown in Figure 1. Analyzing the XRD (Figure 1a), characteristic peaks of MIL-88A were obtained at 2θ = 7.4°, 10.0°, 13.0°, 15.7° and 19.5° which are related to 2θ = 7.4°, 10.0°, 13.0°, 15.7° and 19.5°. The FTIR spectrum identified bands 573, 673, 1390-1595,

3000-3700 cm^{-1} relating to Fe-O vibration, carbonyl group of the organic structure of MIL-88A, symmetric and asymmetric vibrations of the carboxyl group and vibration of the absorbed water molecule.

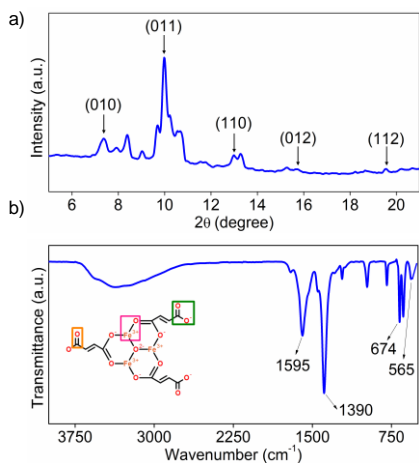


Figure 1. Characterization of MIL-88A: a) XRD and b) FTIR.

Evaluation of membranes: The result for different RB5 degradation processes is shown in Figure 2. Degradation efficiency followed the order: adsorption < photocatalysis heterogeneous < photolysis < Fenton < photo-Fenton processes with degradation (%) of 7.4 < 21.3 < 22 < 26.1 < 100, respectively. As the Photo-Fenton reaction was the most efficient, this process was chosen for membrane regeneration.

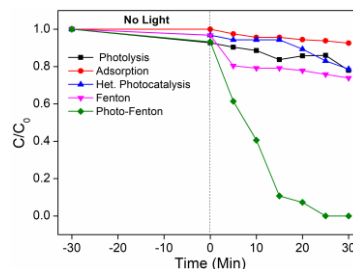


Figure 2. Effect of different RB5 degradation processes.

Membrane recyclability: The average permeation flux was $95.7 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$, with only an 8% reduction after 13 cycles of reuse. The rejection rate of RB5 remained consistently high (100%) during the initial cycles but decreased by 17% in the final cycle. This reduction of the flux and rejection rate can be attributed to surface cracks in the membrane, which caused leaching of MIL-88A during recycling. Nevertheless, the membrane demonstrated the ability to be reused multiple times and efficiently treated 1.3 L of RB5 dye solution.

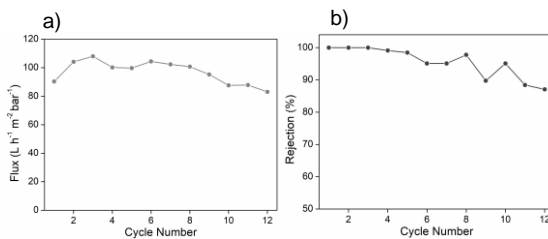


Figure 3. a) Permeation flux and b) rejection of RB5 during 13 recycles.

Conclusions

It was feasible to conclude that the synthesized MIL-88A was successfully synthesized through the performed characterization techniques. The most efficient process for RB5 degradation was the photo-Fenton reaction, achieving 100% degradation after 25 min reaction. Regarding recyclability, the membrane demonstrated the ability to be reused for 13 cycles, maintaining a rejection rate of 87.2% and a permeation flux of $82 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$.

Acknowledgments

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