

ORIGINAL RESEARCH PAPER

Investigation on Polysulfone Blended NH₂-MIL125 (Ti) Membrane for Photocatalytic Degradation of Methylene Blue dye

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ABSTRACT

Membrane hybrid processes represent innovative separation technologies in which each technique complements the advantages and overcomes the challenges of the other. Dye removal from wastewater is an application in which membrane hybrid processes are widely applied. The focus of this study is also on the development of a membrane hybrid process for dye removal from wastewater. Different proportions of NH₂-MIL125(Ti) were embedded in a PSf polymeric membrane through the phase inversion method. The membrane performance was evaluated for the degradation of a Methylene Blue dye under three different light conditions of dark environment, UV, and visible light irradiation. The synthesized membranes were characterized by FTIR, XRD, and FE-SEM measurements. NH₂-MIL125(Ti) nanoparticles were successfully entrapped in the PSf membrane through a simple phase inversion method and the addition of NH₂-MIL125(Ti) to the PSf membrane resulted in the improvement of membrane porosity. Up to 60% of dye degradation was observed with the 1% NH₂-MIL125(Ti)/PSf nanocomposite membrane after 300 minutes of UV light irradiation. Degradation kinetics followed a pseudo-first-order model, indicating possible changes in the membrane properties upon irradiation with simulated solar radiation.

Keywords: Dye removal; Membrane; MOF; Polysulfone; Photocatalyst

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INTRODUCTION

Human demand, consumption, and industrialization increased dye requirement in many industries such as paper, plastic, food, textile, tannery, cosmetics, etc. China, India, and the USA have the highest export rate of textiles around the world [1], [2]. Different types of reactive dyes are highly toxic even in minor concentrations (often less than 1 mg/l) and may cause serious problems for human health and aquatic life due to changing the level of Biological Oxygen Demand (BOD) in water [3], [4]. This issue encouraged

the governments in most countries to enact laws and instructions that prevent the discharge of dye-containing wastewaters into the environment without proper treatments [5], [6].

Methylene Blue (C₁₆H₁₈N₃ClS) is categorized as a cationic dye. MB is widely utilized in textile industries, and its complex structure provides high resistance under intense light and heat irradiation [7]. Wastewaters containing MB, that are being discharged into the environment, typically include the MB concentration range of 10-200 ppm that causes severe damage to the environment and humans health [8] and could release aromatic

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amines such as benzedrine and bethylene, which are carcinogenic and could cause diseases such as gastrointestinal problems, anemia, and profuse sweating [9].

Although numerous methods of dye removal such as chemical, biological and physical techniques have been studied, there is still a gap for high-performance methods which are capable of dye removal from wastewater with high efficiency [10]. Membrane separation is an effective and useful approach due to its low costs, potentials for material recovery, being ecologically friendly, and the removal of various components in a selective manner. However, this technique represents a simple separation function by only transferring pollutants from one phase to another [11], [12]. In recent years, attentions have been attracted to the modified photocatalytic membranes [13]. Photocatalytic reactions could completely degrade organic pollutants. The advantages such as separation and reusability of photocatalysts with low cost and energy, antifouling properties, and fine permeate flux, have made it an efficient method among conventional methods [14], [15]. A combination of membrane separation and the photocatalytic process could be a solution in order to enhance membrane permeability and organic degradation in wastewaters containing hardly-decomposable compounds such as dyes [16]. Several reports have been made in describing the performance of photocatalytic membrane technology for wastewater treatment. For instance, Zioui et al. used photocatalytic modified poly (vinylidene fluoride-trifluoro ethylene) membrane for oily wastewater treatment [17]. It was figured out that the proposed nanocomposite membrane was effective in oil degradation under sunlight irradiation. Kuvarega et al. studied the impacts of enhanced porosity and hydrophilicity on the removal efficiencies of eosin yellow 97% after 4 hours of visible light irradiation [18]. In another study, modifications on the microstructure of photocatalytic membrane by incorporation of N-doped anatase/rutile mixed-phase TiO₂ nanorods improved photocatalytic activity in the degradation of phenol in aqueous solution under UV and visible light irradiation [19].

The photocatalytic process mainly consists of semiconductor catalysts such as ZnO, TiO₂, etc. The recombination of electron-hole and induced electron with sufficient energetic photons(which are received from UV or visible light sources),

affects the dye degradation rate. The properties and structure of photocatalysts such as band-gap energy(which is the most important factor), particle size distribution, crystal composition, porosity, and surface area, considerably influence the photocatalytic efficiency [20]. The most widely used photocatalyst in photocatalytic membrane reactor (PMR) systems is TiO₂, due to its distinctive characteristics such as nontoxicity, desirable chemical stability and activity, and low price [21].

Metal-organic frameworks (MOFs) are a class of materials in which metal ions/clusters interact with each other through organic bonds to form porous structures. They have the potential to be used in various applications, especially in photocatalysis, which is the main interest of the current research [22]. The NH₂-MIL125(Ti) is a MOF form with cyclic Ti₈O₈(OH)₄ oxoclusters and 2-aminoterephthalate ligands and has shown a great affinity to adsorption inbound visible light in the electromagnetic spectrum due to its amino-functionalized structure [23].

The PSf membrane has been widely used as a commercial membrane because of its advantages such as high glass-transition temperature (T_g), high pH tolerance, low price, and noticeable permeability. However, this membrane has some disadvantages due to its inherent hydrophobic nature and membrane fouling which results in flux decline and increasing demand for filtration energy [24], [25]. UV irradiation, blending with hydrophilic nanoparticles, graft polymerization, and spin coating are examples of the solutions that have been suggested, in order to overcome the inherent hydrophobicity of polysulfone membrane [18]. Among all these solutions, the blending of TiO₂ with PSf membrane has led to a significantly positive impact on the surface hydrophilicity and promoted the permeate flux [26], [27]. MOF usage in the polysulfone matrix, while facilitating its separation from the degraded pollutant solution, helps to use it in future studies such as in a photocatalytic membrane reactor system. This research focuses on NH₂-MIL125(Ti)/PSf membrane preparation which is employed subsequently for the degradation of MB dye in wastewater. The NH₂-MIL125(Ti)/PSf nanocomposite was characterized by FTIR, XRD, and FESEM. Finally, the nanocomposite's performance for MB removal from synthetic wastewater was studied, under visible light, UV light irradiation, and in a dark environment.

Table 1. Composition of synthesized membrane

Composite membrane	Amount of Nano (g)	MOF/PSf percentage %
PSf	0	0
PSfM 0.2	0.038	0.2
PSfM 0.5	0.095	0.5
PSfM 1	0.19	1

MATERIALS AND METHODS

Methanol (CH₃OH, CAS No. 67-56-1), Dimethylformamide (DMF) (C₃H₇NO, CAS No. 68-12-2), N-Methyl-2-Pyrrolidone (NMP) (C₅H₉NO, CAS No. 872-50-4), and Polyethylene glycol 400 (C_{2n}H_{4n+2}O_{n+1}, CAS NO. 25322-68-3) were supplied by Merck, Germany. Titanium isopropoxide (C₁₂H₂₈O₄Ti, CAS No. 546-68-9) was obtained from Alfa Aesar, 2-aminoterephthalic acid (C₈H₇NO₄, CAS No. 10312-55-7) was supplied by Sigma Aldrich, and polysulfone (C₈₁H₆₆O₁₂S₃X₂, CAS No. 25135-51-7) was provided by BASF. Methylene Blue (MB) (C₁₆H₁₈ClN₃S) was used as a model compound. It was supplied by Sigma Aldrich. The dye solution was prepared using distilled water.

Characterization of the NH₂-MIL125(Ti)/PSf nanocomposite

Fourier transform infrared (FTIR) spectroscopy was performed via a Varian 670 FTIR spectrometer recorded at the resolution between 400 and 4000 cm⁻¹. The sample crystallinity was determined by using X-ray diffractometer (XRD) Philips PW 1730 radiation of wavelength 1.540598 Å at 40 kV and 30 mA. The diffracted intensity was measured by scanning range of 2θ = 5 – 80° with a step speed of 3°.min⁻¹. Field-emission scanning electron microscopy (FE-SEM) FEI NOVA NanoSEM 450 equipped with an energy dispersive X-ray spectrum (EDS) was used to investigate the surface morphology of the NH₂-MIL125(Ti) and NH₂-MIL125(Ti)/PSf membrane.

EXPERIMENTAL

Preparation of NH₂-MIL125(Ti)

The synthesis of the MOF nanoparticles was performed according to the proposed method by Nasalevich et al. as following [28]. First, the mixture of 40 mL dimethylformamide and 10 mL methanol was stirred at room temperature while adding 2.86 g of 2-aminoterephthalic acid to the mixture. After homogenization, 2.86 g of titanium

isopropoxide was added slowly (to prevent aggregation) and the mixture was stirred, for a few hours. Afterward, the mixture was placed in a Teflon liner inserted in a stainless steel autoclave reactor and the mixture was heated at 110 °C in an oven for 72 hours. Subsequently, after being cooled in room temperature, the resulting mixture was filtered and washed with a sufficient amount of dimethylformamide (50 mL of DMF per 1 g of product) in order to remove residual linker for 48 hours. Later on, the same procedure was repeated twice using methanol instead of DMF in order to exchange the DMF within the pores. Finally, the resulting solid was dried in dry air with a temperature of 100°C [28].

Preparation of NH₂-MIL125(Ti)/PSf

First, a specific amount of N-Methyl-2-pyrrolidone (NMP) was stirred for 30 minutes and then placed in an ultrasonic bath for further homogenization for another 30 minutes. Afterward, the mixture was stirred again while 19 g of PSf polymers were added gradually. In this regard, the polyethylene glycol (PEG) 400 was used in order to increase the porosity/permeability in the membrane structure, and 4.5 mL of it was added to the solution for membrane fabrication. In order to prevent the generation of bubbles in the polymer solution, the container of the polymer solution was placed in water at 80 °C for 24 hours. NH₂-MIL125(Ti)/PSf membrane with compositions of 0, 0.2, 0.5 and 1 wt. % were denoted as PSf, PSfM0.2, PSfM0.5, and PSfM1 respectively regarding the amount of MOF which is shown in Table 1.

After preparing the solution, the phase inversion process was carried out to fabricate a membrane with a specific thickness [29]. Subsequently, the casting solution was cast onto flat glass plates with 300 μm thickness and the resulted film was submerged into distilled water at 25 °C following the initial phase separation and membrane solidification. Later on, the membrane was preserved in fresh distilled water for 24 h in

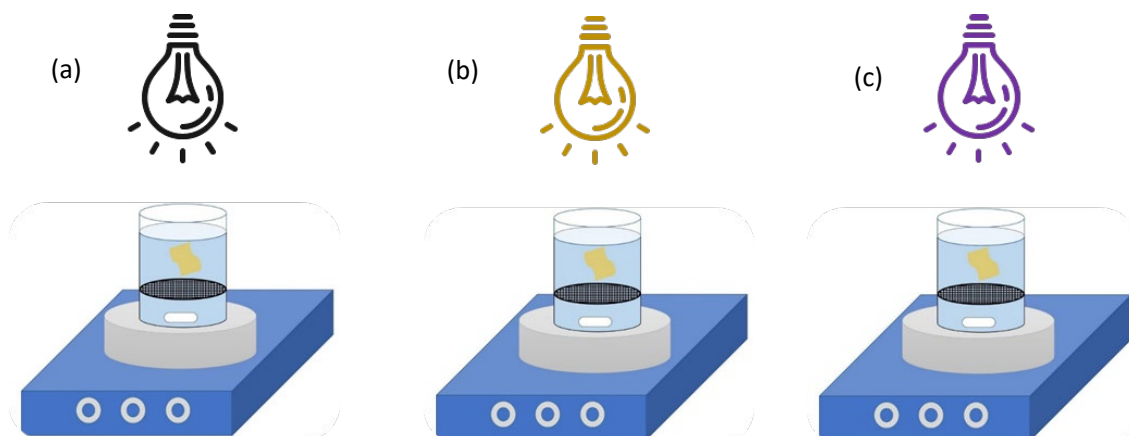


Fig. 1. Schematic representation of the photodegradation setup in (a) dark, (b) Visible light and (c) UV light ambient

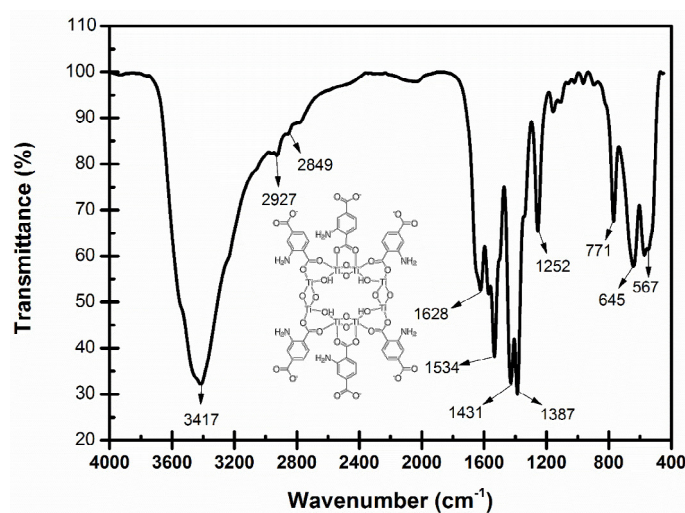


Fig. 2. FTIR spectra for NH₂-MIL125(Ti) MOF

order to ensure full phase inversion [30]. As the solvent is removed from the film layer, flat sheet polymeric membrane would be achieved.

Evaluation of photocatalytic activity

The photocatalytic performance of the fabricated membranes was investigated by measuring the degradation rate of Methylene Blue (MB) in darkness, visible light, and under UV irradiation. A strip (8 cm x 8 cm) of the polymeric membrane was suspended in 100 mL of MB solution (10 ppm) under the mentioned light conditions (Fig. 1). The UV irradiation was obtained from an ultraviolet (UVC) lamp (Philips Electronics, Poland, λ = 253.7 nm, 6 W). On the other hand, the visible light irradiation is obtained from white light-emitting diode (LED) floodlight (EDC, Iran, λ > 420 nm, 6 W).

Prior to the photocatalytic reactions, the solutions were stirred on a magnet stirrer in the dark environment for an hour in order to achieve adsorption/desorption equilibrium. 2mL aliquots of the dye solution, that is being treated, were withdrawn using a disposable syringe at 60 minutes intervals for 300 minutes. Variations in the concentration of MB under illumination were monitored using a UV-Vis spectrophotometer (2120UV PLUS, Optizen) at λ = 665nm.

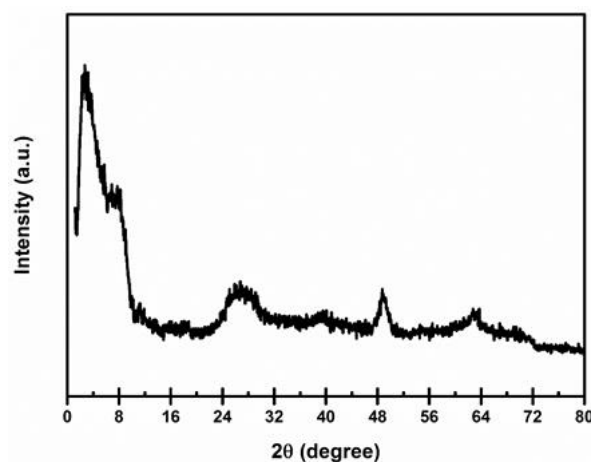
RESULTS AND DISCUSSION

Characterization of NH₂-MIL125(Ti)

The chemical structure of NH₂-MIL125(Ti) was analyzed by FT-IR (Fig. 2). The spectra were characterized by high-intensity peaks in the region 4000 cm⁻¹ to 400 cm⁻¹. Regarding the results of

Table 2. FTIR peak assignments

Peak Position (cm ⁻¹)	Peak Assignment
3417	tensile vibration of the O-H and N-H groups
2927	Asymmetric tensile vibrations of the C-H bands in the -CH ₂ structure
2849	symmetric tensile vibrations of the C-H bands in the -CH ₂ structure
1628	flexural vibration of N-H bonds
1534	carboxylate ligands
1431	carboxylate ligands
1387	oscillatory vibration of -CH ₂ groups
1252	tensile vibration of C-N bonds at aromatic amines
800-400	O-Ti-O vibration

Fig. 3. XRD spectrum of the NH₂-MIL125(Ti)

the FTIR test, it could be concluded that NH₂-MIL125(Ti) is existing in the studied system.

Specific bands and their assignments are summarized in Table 2 [31-33].

The crystal structure of NH₂-MIL125 (Ti) was identified by XRD (Fig. 3). It could be observed that NH₂-MIL125(Ti) was mainly amorphous which is in agreement with FE-SEM observations and presented one prominent peak at $2\theta = 3^\circ$ [30]. Peaks at low diffraction pattern angles, 2θ value of 3 and 10 degrees respectively corresponding to the (101) and (002) planes, and peaks at four prominent diffractions at $2\theta = 20^\circ, 28^\circ, 48^\circ,$ and 63° , confirm the formation of the NH₂-MIL125(Ti) phase in the structure [34]. This structure contains chains of μ -OH corner-sharing TiO₆ octahedral, which are interconnected by NH₂-BDC molecules in order to form three-dimensional pores [35].

Fig. 4 shows the results of investigation on the surface morphology of the NH₂-MIL125(Ti) by the FE-SEM test. According to the results, the surface of the sample (at 1000x magnification) includes a

sheet of aggregated particles, which is more visible in part (c). Due to the surface-to-volume ratio of these nanoparticles and their high surface energy, they are clinging together and forming clusters in order to achieve a more stable state of the nanoparticles.

Characterization of NH₂-MIL125(Ti)/PSf membrane

The FE-SEM images of the NH₂-MIL125(Ti)/PSf membrane system containing different amounts (0, 0.2, 0.5, and 1%) of MOF are shown in Fig. 5. As shown in Fig. 5(a), no particle is visible in the pure PSf membrane sample and a large clean surface is obvious in the image. By applying MOF into the polymer matrix, the surface morphology of the nanocomposite changes, and particles of different dimensions could be observed on the surface of the samples. Regarding Fig. 5, by increasing the percentage of MOF in the nanocomposite, the number and the size of the particles, presenting on the polymer surface, have increased so that the average size of these particles became almost 32.4

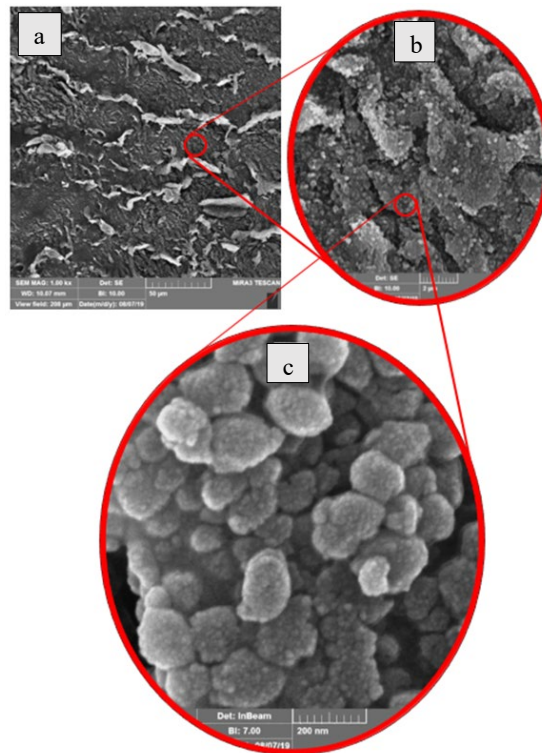


Fig. 4. FESEM images morphology of the NH₂-MIL125(Ti) surface investigated at three different magnifications (a) 1000, (b) 15000 and (c) 200000 times

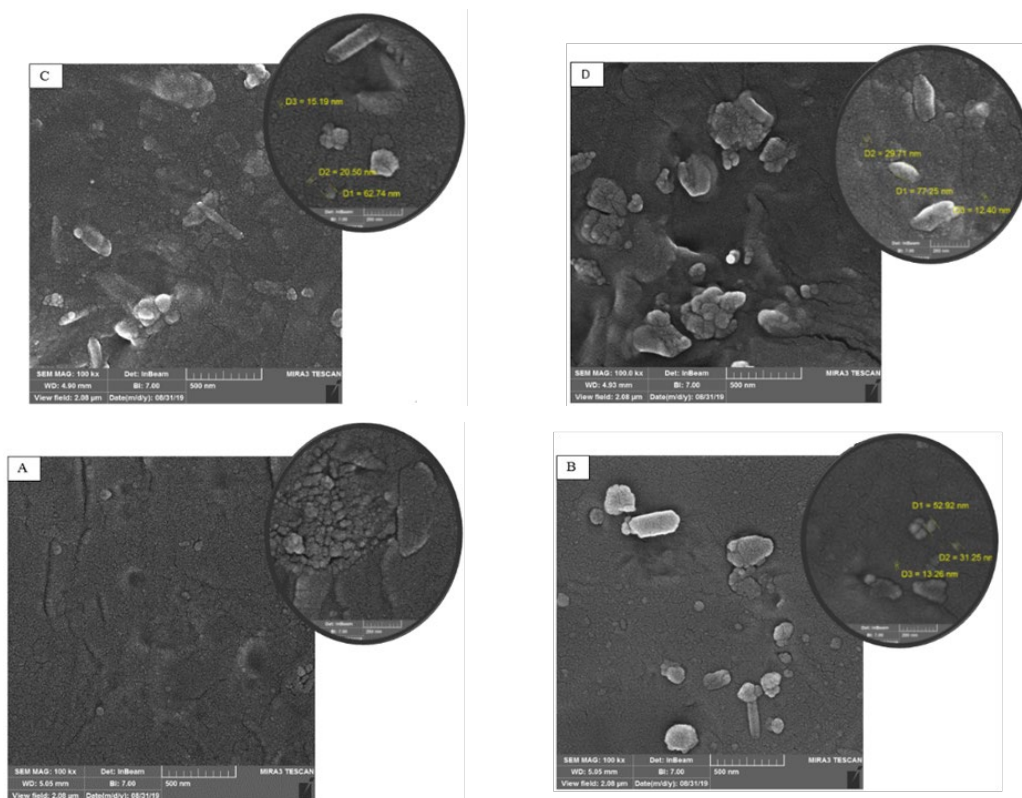


Fig. 5.A. (a) FESEM images of PSf membrane sample and PSf membrane sample containing (b) 0.2, (c) 0.5 and (d) 1% MOF

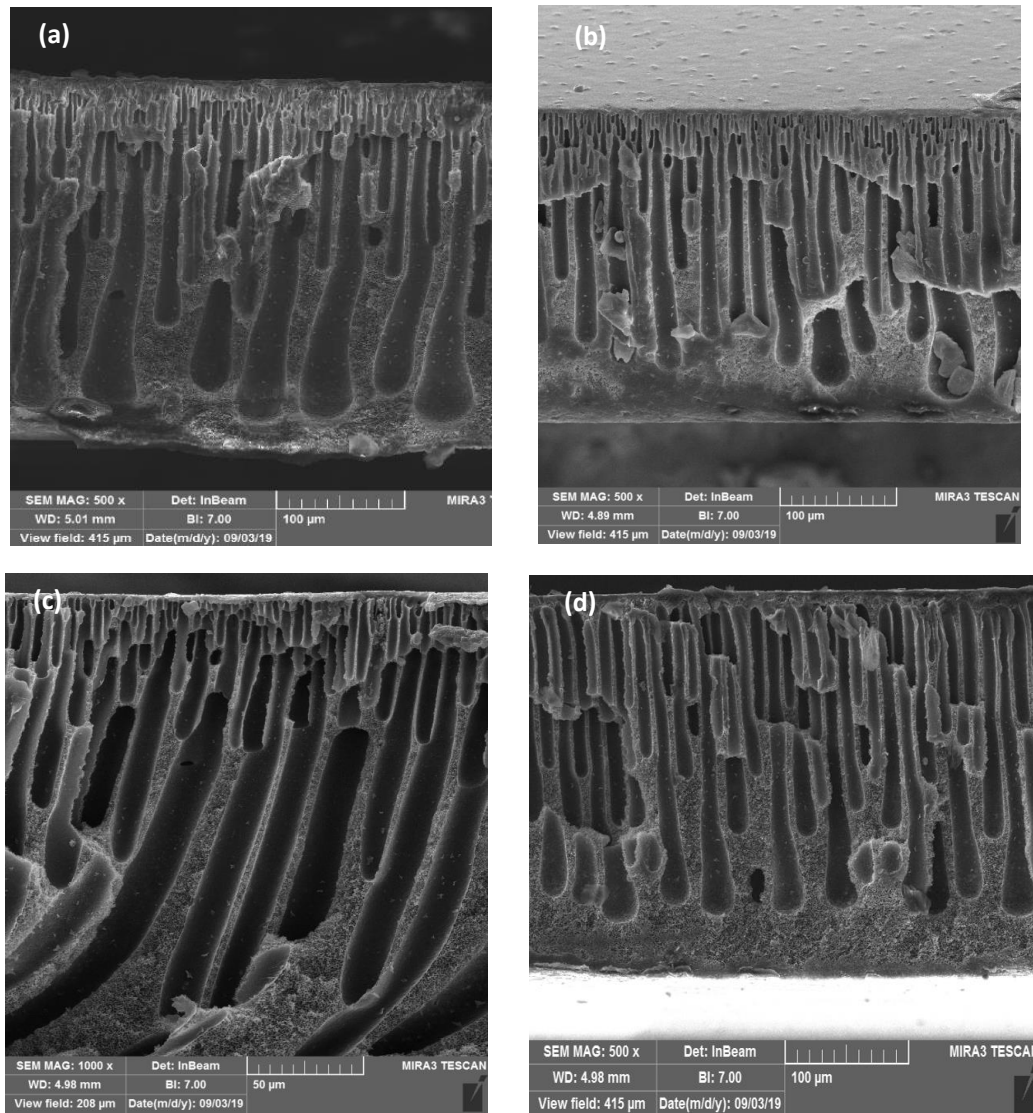


Fig. 5.B. SEM images from the cross-section morphology of NH₂-MIL125(Ti)/PSf membrane: a) PSf b) PSfM0.2 c) PSfM0.5 d) PSfM1

nm in the PSf sample. By increasing the composition of MOF in the PSf polymer matrix, the number and size of these particles have increased and reached a size of 38.8 nm. These results indicate that despite the increase in the percentage of MOF from 0.2 to 0.5 wt. %, no significant effects have been made on particle agglomeration, and the dispersal performance was respectably at 0.5 wt. %. However, by a further increase in the MOF percentage of the polysulfonate structure, particle scattering was affected and as the particles are agglomerating within the polymer matrix structure, they reach a growth rate of about 20%. This mode of clustering

in the low magnified image is also evident in Fig. 5(d). Particle agglomeration could affect the final characteristics of the system and change some of the nanocomposites properties.

Fig. 5.B. shows the images from the cross-section of the NH₂-MIL125(Ti)/PSf membrane with different compositions. It could be observed that the density and quantity of the membrane pore have gradually enlarged by increasing the concentration of NH₂-MIL125(Ti) in the membrane. From this cross-section morphology, it could be observed that all membranes have a homogeneous porous internal structure. Moreover,

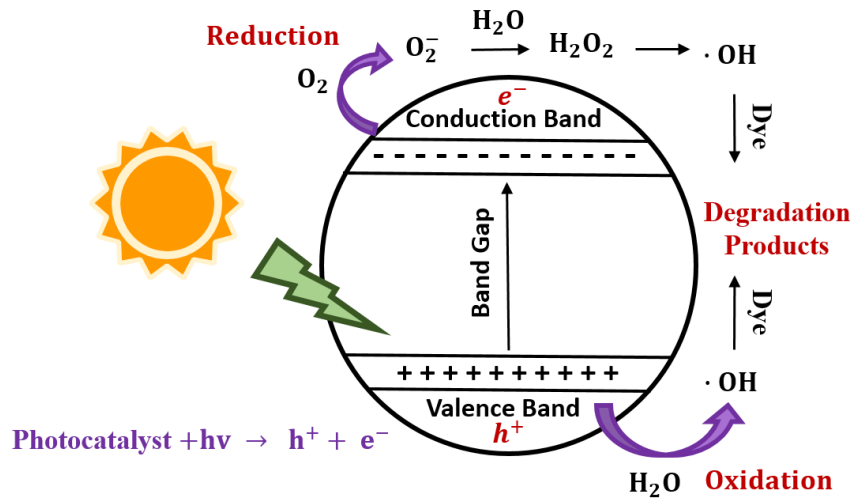
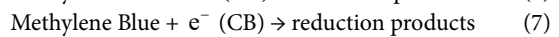
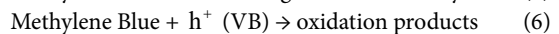
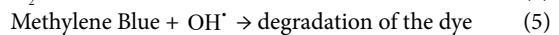
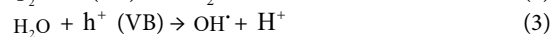
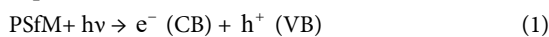


Fig. 6. Proposed mechanism for photocatalytic degradation of Methylene Blue dye over NH₂-MIL125(Ti)/Polysulfone membrane under irradiation

the sponge-like bottom layer, intermediate layer, and top skin layer show a typical asymmetrical structure. On the other hand, the presence of NH₂-MIL125(Ti) in the membrane structure plays a significant role in hydrophilic characteristics and photocatalytic activity of the membrane surface.

The photocatalytic performance of NH₂-MIL125(Ti)

The details of the reactions and mechanisms of MOF in the PSf polymer matrix for MB's photocatalytic degradation are presented in Fig. 6. When MOF is exposed to visible and UV light irradiation with energy equal or greater than their band gaps, the electrons (e⁻) are excited by photo-induced from the highest occupied molecular orbital (HOMO) (6.4 eV) to the lowest unoccupied molecular orbital (LUMO) (3.8 eV), thus leaving the holes (h⁺) in the valence band. The excited electrons (e⁻) might be directly entrapped by the molecular oxygen dissolved in solution in order to form superoxide radicals (O₂⁻). The produced holes (h⁺) are reacted with water molecules or hydroxyl ions (-OH) in order to produce hydroxyl radicals (OH[•]), which oxidize and degrade the dye molecules. In addition, the photo-induced holes (h⁺) could directly oxidize the MB molecules as well. O₂ reduction and H₂O oxidation could generate O₂⁻ and OH[•] [36], [37]. The reactions at the surface of the photocatalyst initiating the degradation of MB dye could be expressed as follows:



Photodegradation kinetics follow the Langmuir-Hinshelwood (L-H) model (Fig. 7(c), 8(c), 9(c)) where monolayer adsorption takes place on the nanoparticles' surfaces [38]. The reaction rate depends on the concentration of the pollutant according to Eq. 8:

$$r = \frac{dC}{dt} = -\frac{kKC}{1+KC} \quad (8)$$

where r is the rate of the reaction, C is the dye concentration in the solution, t is time, k is the reaction constant and K is the adsorption equilibrium factor for the pollutant on the photocatalyst surface. Assuming KC to be negligible, the equation could then be simplified to Eq. 9:

$$\ln \frac{C}{C_0} = \frac{dC}{dt} = -k_{app}t \quad (9)$$

where C₀ is the initial concentration of dye, C is the concentration at time t and k_{app} is the apparent reaction constant [39].

The photocatalytic activity of NH₂-MIL125(Ti) nanoparticles for MB dye removal, was investigated under visible light [40] (Fig. 7). The effects of different

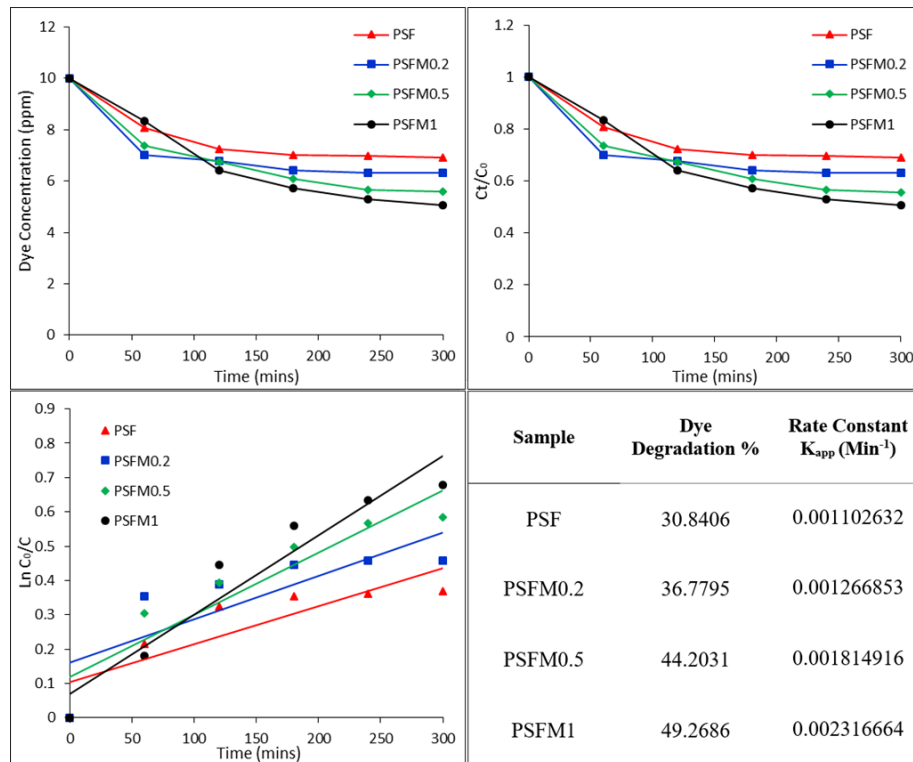


Fig. 7. Photocatalytic activity of the membranes under Visible irradiation; (a) dye degradation, (b) normalized dye degradation, (c) degradation kinetics, (d) table of % degradation and rate constants

NH₂-MIL125(Ti)/PSf membrane compositions on Methylene Blue dye removal over 5 hours and under visible light is presented in Fig. 7. As shown in Fig. 7 (a,b), the percentages of dye removal for all PSfM samples are higher than the pure PSf membrane. PSfM1 shows the highest dye removal efficiency after 5 hours, and PSfM0.2 and PSfM0.5 became stable, respectively after 3 and 4 hours. According to Fig. 7(d), the rate constant of pure PSf membrane was lower (0.001102632 min⁻¹) than the loaded nanoparticle membranes, with PSfM1 showing the highest degradation rate (0.002316664 min⁻¹). The results indicate that under visible light irradiation, adding excess amounts of NH₂-MIL125(Ti) nanoparticles causes severe agglomeration which decreases the active sites of the membrane [41].

Fig. 8 shows the effects of membrane composition on the removal of MB dye over 5 hours under UV irradiation. The rate constant of pure PSf membrane was lower than that of the nanoparticle loaded membranes, with PSfM1 showing the highest degradation rate (0.002757 min⁻¹) (Fig. 8(d)). MB dye would be adsorbed on the membrane surface and neutralizes the negative charges on the surface of the membrane. Also, under the UV light

irradiation, the photocatalytic activity takes place inside the membrane which may lead to further degradation of MB. After a while, the adsorption sites of the membrane surface would be covered and the electrostatic adsorption forces between the membrane surface and MB becomes weaker which results in a decrease in the photocatalyst performance of the membrane [42].

Fig. 9 shows the removal of MB in the dark environment for 5 hours. In the dark environment experiment, the dye removal percentage was reduced down to 17% and 38% compared to the visible and UV irradiation, respectively. Fig. 9(a) shows that the removal of MB in the first 2 hours has an upgoing trend and afterward it becomes stable. In the dark environment, the rate constant of pure PSf membrane was lower (0.000957 min⁻¹) than that of the nanoparticle-loaded membranes, with PSfM1 showing the highest degradation rate (0.001337 min⁻¹) (Fig. 9(d)). In the dark environment, there are no photons in order to activate the electrons. It leads to the dominance of adsorption in the dye degradation process which results in an adsorption equilibrium [40]. According to Fig. 9 at the first 60 minutes of the adsorption process, dye molecules have a high

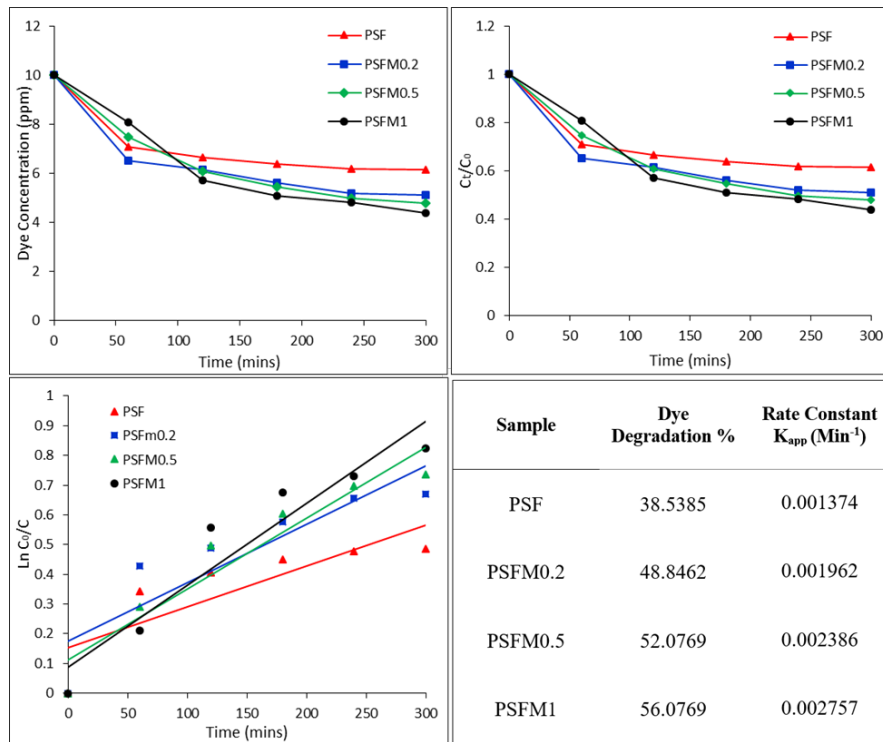


Fig. 8. Photocatalytic activity of the membranes under UV irradiation; (a) dye degradation, (b) normalized dye degradation, (c) degradation kinetics, (d) table of % degradation and rate constants

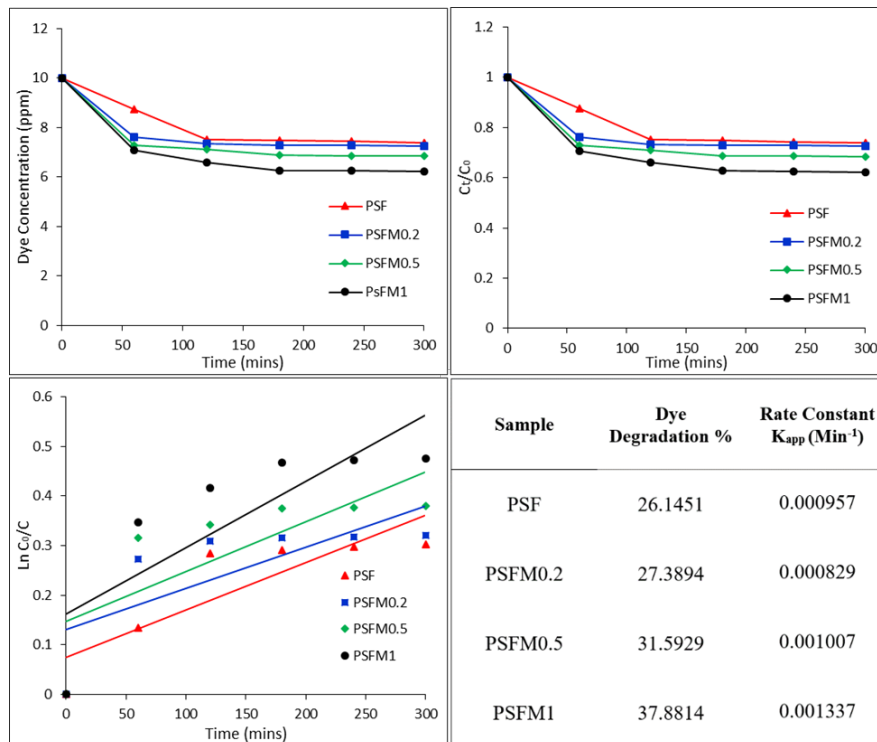


Fig. 9. Photocatalytic activity of the membranes in the Dark environment; (a) dye degradation, (b) normalized dye degradation, (c) degradation kinetics, (d) table of % degradation and rate constants

tendency to be adsorbed onto the membrane's surface; however, after a while, this tendency would decrease and dye degradation rate gets almost stable [10].

From all of the above figures, it could be concluded that the entrapment by MOF, improved the photocatalytic performance of the PSf membranes. On the other hand, the results have showed that the reaction rate was low in the first hour and increased gradually overtime. This process could be explained by the hydrophilic properties of the membrane. As the physical and chemical modifications of the polymer are taking place, and polymer is being exposed to the absorption of electromagnetic radiation in the presence of oxygen molecules, short chains of d-sulfonic acid molecules would be released. Sulfonic acids are surfactants that significantly reduce the contact angle of the membrane and reduce the repulsion between the surface of the membrane and dye, resulting in the increase of dye penetration into the membrane [43].

CONCLUSIONS

The paper studied the phase inversion embedment of NH₂-MIL125(Ti) in PSf membranes for the photocatalytic removal of Methylene Blue from synthesized wastewater. The effects of NH₂-MIL125(Ti) dosage and various irradiations on membrane performance were investigated. The entrapment of NH₂-MIL125(Ti) into PSf membranes resulted in an enhancement of the membrane photoactivity, porosity, and hydrophilicity without compromising membrane integrity. Up to 60% of Methylene blue dye was removed after five hours of UV light irradiation of the membrane. By simple comparison, it was observed that there is a slight difference between the dye removal efficiency of being exposed to visible light on one hand and UV light irradiation on the other hand, which conducts us to prefer the visible light due to the availability of this irradiation source and not causing damage to the membrane structure. Unlike free photocatalytic nanoparticles, the membrane could easily be taken out of the system and be used again which significantly reduces the post-treatment costs. Studying the use of this membrane in the membrane system and its performance, are considered to be addressed in future work.

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CONFLICT OF INTEREST

Author declares no conflict of interest.

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