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Fabrication of Tight-Ultrafiltration Membrane by Combining Zif-8/Gypsum Additives to Enhance Removal of Organic Dye Substances

Alifia Putri Salsabila[1], Faaizah Azmi Nazhiifah[1], Kanaya Lintang Salsabila[1], Devina Ammadhea Amanda[1], Michelle Shaumy Sahfa[1], Heru Susanto[1,2]

[1]Chemical Engineering Department, Engineering Faculty, Universitas Diponegoro, Jl. Prof. Soedarto, SH, Tembalang, Semarang, Indonesia, [2]Membrane Research Centre, Universitas Diponegoro, Jl. Prof. Soedarto, SH, Tembalang, Semarang, Indonesia

Corresponding Author Email: bsalsa716@gmail.com

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Abstract

Organic dyes that have been used in many industries contain chromophore (azo group, aromatic rings) which is hard to degrade. Therefore, wastewater containing organic dyes poses a serious threat to aquatic ecosystems and human health. Various techniques have been developed to remove organic coloring agents to alleviate the increasing concern of non-degradable organic dyes. Adsorption using membranes is considered the most economical and efficient method to control water pollution from dyes. In this research, to further enhance the adsorption capacity of organic dyes on the membrane, a new strategy was developed involving in-situ blending of ZIF-8/gypsum during the dope solution preparation and membrane printing processes. Gypsum, also combined with the polymer matrix of the membrane to create a hierarchical membrane with large adsorption capacity and separation of dyes. Based on the experiment that has been carried out, it is found that the water absorption rate and membrane porosity tended to increase as the difference measured between dry and wet weight of membrane after soaking gets bigger and higher amount of gypsum added leads to higher flux in tested membrane. A specific membrane composition, denoted as M4, demonstrates optimal performance with a blend of PVDF (polyvinylidene fluoride) at 11%, ZIF-8 (Zeolitic Imidazolate Framework-8) at 0.3%, and gypsum at 7%. This formulation results in a permeability of 58.8 L/m2.h.bar and a rejection rate of 34.21%. These outcomes align well with the observed trends in membrane porosity and surface hydrophilicity which incorporating ZIF-8 membrane exhibit antifouling properties, demonstrating effective resistance to fouling on the membrane surface. Eventually, these developed membranes show promise for extending the use of MOF-related materials and applications in the treatment of dye-containing wastewater, contributing to the production of cleaner water.

Keywords: PVDF, Ultrafiltration Membrane, ZIF-8, Gypsum, Dyes Treatment

Introduction

Organic dyes have been widely used in various industries such as textiles, printing, cosmetics, etc (Ezugbe and Rathilal, 2020). Since the chromophores (azo groups, aromatic rings) in most organic dyes are quite stable and not easily converted into small molecules Bhat and Gogate (2021), it is difficult to achieve rapid degradation of organic dyes (El-Sayed, 2020). Therefore, wastewater containing organic dyes poses a serious threat to aquatic ecosystems and human health. To reduce the increasing concerns of non-degradable organic dyes, various techniques, including adsorption Feng et al (2022), membrane separation Chen et al (2020), ion exchange, reverse osmosis/electrodialysis, photocatalytic degradation Housaindokht et al (2022), and others, have been developed to remove organic dyes.

Adsorption is an efficient and economical method for purifying wastewater (Fang et al., 2022). Most of the adsorbents used to remove pollutants in water, such as activated carbon (He et al., 2020), natural zeolites, graphene Jing et al (2021) and metal-organic frameworks Jin et al (2020) are particulate materials or nano powders. Although these particulate or nanoscale adsorbents are easy to prepare and show great adsorption and fast adsorption capacity towards organic dyes, after their use it is difficult to effectively separate these adsorbents from water, which easily causes secondary pollution. Compared with these particulate adsorbents, tight-ultrafiltration (TUF) membrane technology has received widespread attention in the purification of organic dye-polluted wastewater, mainly because of its tunable porosity, large specific surface area, desirable mechanical properties, as well as the density of high reactive sites (Chen et al., 2020).

Among the various materials used for TUF membrane fabrication, thermoplastic polymers, polyvinyl alcohol (PVA) Wang et al (2021), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) (Mavukkandy et al., 2022), have received extensive attention due to their physicochemical stability as well as film-forming properties. To further increase the adsorption capacity of organic dyes on the membrane, gypsum is also combined with the membrane polymer matrix to create a hierarchical membrane with a large dye adsorption and separation capacity. For example, (Rahman et al., 2015). performed rapid adsorption and selective separation of methyl blue cationic dye from aqueous solution using gypsum. Hassan et al (2021) precipitated gypsum to remove water-soluble chlorazole yellow and methyl blue. Gypsum can also be used to remove reactive red 1 (RR1) as done by (Obunwo et al., 2012).

Although improvements in dye removal have been obtained, the long-term stability of these membranes still requires further optimization. More specifically, gypsum inserted into the membrane can be partially degraded when the membrane is used, considering that gypsum has decomposable properties. Therefore, it is necessary to develop an easy protocol to prepare TUF membranes with controllable adsorption sites and good organic dye removal capacity.

Metal organic frameworks (MOFs), such as zeolitic imidazole frameworks (ZIFs), exhibit tunable molecular structures, excellent mechanical properties, resistance to high temperatures and chemicals, and biocompatibility. ZIF-8 can be used to hold controllable water selective permeation channels to increase water permeation. Interestingly, ZIF-8 may also contribute to the intrinsic affinity for the dye. In this study, a new strategy was developed involving in-situ blending of ZIF-8/gypsum during the dope solution preparation and membrane printing processes.

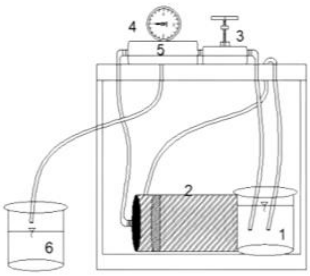
Method

Time and Place of Implementation

The research was carried out over a period of 4 months at the Membrane Research Center (MeR-C) Laboratory at Diponegoro University (UNDIP). Instrumentation analysis tests are carried out at the UNDIP Integrated Laboratory (UPT).

Material and Tools

The materials used for TUF membranes are from PVDF, ZIF-8, gypsum, and gluteraldehyde (GA) as the main raw materials for membrane modification, methylene blue as impurity solution, NMP as a solvent, and distilled water as a non-solvent. Research materials purchased from Merck KGaA. (Darmstadt, Germany). Meanwhile, the equipment includes a beaker glass, magnetic stirrer, analytical scale lab, integrated crossflow ultrafiltration, oven, UV lamp, screw micrometer, measuring cup, dropper pipette, and various instrumentation tools for testing membrane characteristics.



Known:
1. Methylene blue feed solution
2. Pump
3. Pressure control
4. Barometer
5. Membrane placement site
6. Permeat

Figure 1. A set of crossflow ultrafiltration instruments

Variables

Fixed variables include TUF membrane type (PVDF), drying temperature (60^{o}C), filtration pressure (2 bar), and methylene blue concentrations (100 ppm). Variables changed included gypsum concentration (3, 5, and 7) wt%, ZIF-8 concentration (0 and 0,3) wt%, and GA concentration (0 and 1) wt%.

Membrane Modification

The TUF PVDF membrane was modified by blending with gypsum and crosslinking GA which was prepared via Nonsolvent-induced phase separation (NIPS). Specifically, the membrane is soaked in distilled water for 24 hours. The modified membrane will be dried in an oven at a temperature of 60^{o}C. The membrane will be stored in ziplock packaging until next use. Membrane modifications are more fully explained in Tables 1 and 2.

Table 1
Concentrations of TUF membrane modification

Membrane Code	PVDF (wt%)	ZIF-8 (wt%)	Gypsum (wt%)	GA (wt%)
M1	11	0,3	0	0
M2	11	0,3	3	0
M3	11	0,3	5	0
M4	11	0,3	7	0
M5	11	0,3	5	1
M6	11	0	0	0

Membrane Characterization

Membranes were characterized in terms of morphology, composition, hydrophilicity and membrane roughness using various instrumentation. The morphology and composition on the surface and cross sections before and after separation of MB was analyzed using Scanning Electron Microscopy (SEM) (EDX Spectroscopy, JEOL-JSM-6510LA, Japan). To identify the chemical components of the membranes made, all membranes were analyzed using a Fourier transform infrared (FT-IR spectrometer, PerkinElmer, United States) equipped with a total reflectance below 4 cm^{-1} resolution. The wave number range of 400–4000 cm^{-1} was scanned 16 times, with a scan speed of 1 minute/scan. The permeate was collected every 5 minutes for 60 minutes and the dye concentration was determined using a UV-Vis spectrophotometer. Dye rejection ratio is used as a study of rejection and anti-clogging phenomena. Surface hydrophilicity was evaluated based on Static and Dynamic CA data using water contact angle measurements (OCA, Dataphysics Instrument GmbH, Germany). Where 6 µl of distilled water was dropped on the membrane surface and an adapted digital microscope captured images of the droplets.

Membrane Performance and Durability

Membrane performance was determined through direct filtration tests from MB. Homemade crossflow ultrafiltration equipment was used to perform membrane filtration as shown in Figure 1. Before measurement, the membrane (d= 4.2 cm) was compacted with distilled water at a pressure of 1 bar for 15 minutes, and then the filtered water mass was taken every 5 minutes. once for 15 minutes as the value of pure water permeation. Then the feed water was replaced with 0,5 L of MB solution (100 ppm). The permeate is collected and weighed on an analytical balance, while the concentrate is returned to the feed water. Permeate was collected every 5 minutes for 60 minutes. The membrane was then rinsed for an additional 15 minutes with pure water. Pure water permeability (PWP) and MB rejection (%R) were measured using Equations 1 and 2.

$$\mathrm{PWP} = \frac{\mathrm{V}}{\mathrm{A\ x\ t\ x\ \Delta P}} \qquad (1)$$

$$\mathrm{R} = \left(1 - \frac{\mathrm{C_p}}{\mathrm{C_f}}\right) \mathrm{x}\ 100\% \qquad (2)$$

where, V, A, and ΔP represent the volume (L) of permeate at a certain time t (hour), membrane filtration area (m^2), and transmembrane pressure (bar), respectively. Furthermore, Cp and Cf are the concentrations of MB in the feed and permeate, respectively.

The membrane with the best modification is determined based on flux filtration performance. Then, the membrane with the best modification was filtrated 4 times in cycles as was done in the previous stage with the aim of determining the membrane's ability to be reused, its durability and stability. After recharacterization, analyze whether or not there are changes in the characteristics of the membrane in the form of durability and ability to reuse the membrane.

Result and Discussion

Effect of PVDF and Gypsum Concentration on The Membrane

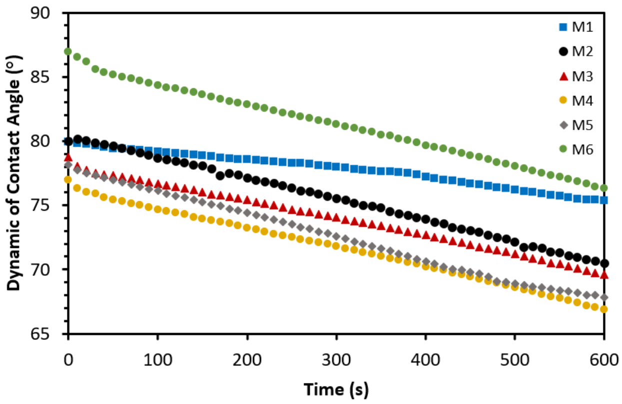


Figure 2. Static and dynamic contact angles

The contact angle, used to measure the interaction between the membrane surface and water droplets, plays a key role in determining the hydrophilicity of the membrane. The membrane can be categorized as hydrophobic if θ ≥ 90°, indicating that water droplets do not spread well on the membrane surface. Conversely, if θ ≤ 90°, the membrane can be considered hydrophilic, indicating that water droplets tend to spread well on the membrane surface (Jhaveri & Murthy, 2016).

In this study, it was found that after modification with gypsum, there was a decrease. This indicates that gypsum has the ability to enhance the hydrophilicity of the membrane (Zhang, H., & Zhao, X., 2023). Gypsum has characteristics that support affinity for water and allow the formation of hydrogen bonds between water molecules and the membrane surface (Min et al., 2018). As a result, this leads to stronger adhesion between water and the membrane. Thus, membrane modification with gypsum has resulted in an improvement in the membrane's ability to interact with water. These findings suggest the potential of how membrane modification with specific materials can alter the hydrophilicity of the membrane and enhance its performance in specific applications.

The contact angle results for membrane M6 show the largest contact angle, which is 76.29°. TUF membrane with the addition of gypsum will increase its hydrophilic properties, as evidenced by the decrease in the contact angle values for membranes M2, M3, and M4, which are 70.47°, 69.61°, and 66.85°, respectively (Figure 2). The decrease in contact angle may be caused by gypsum interacting with water, forming hydrogen bonds that further attach water to the membrane surface.

Effect of Gypsum Modification on TUF Membrane Performance

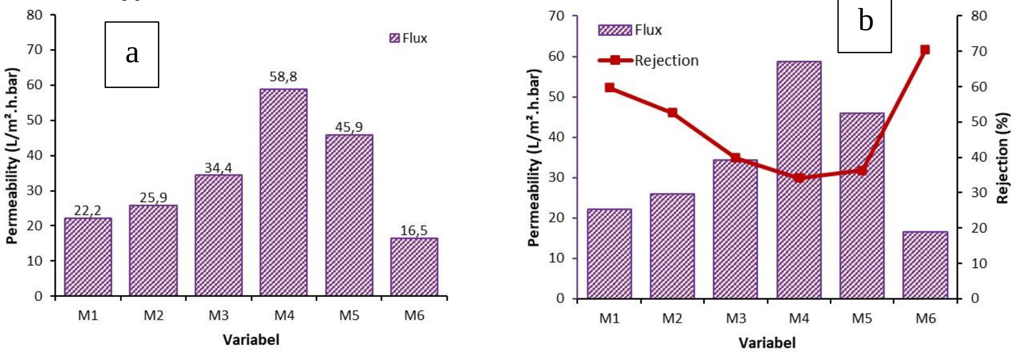


Figure 3. Membrane performance (a) Pure water permeability and (b) water flux and BSA rejection

Permeability (Lp) is the ability to allow pure water to pass through the membrane at the operating pressure of the membrane. The permeability value is obtained from the slope of the flux graph against the operating pressure. The membrane's ability to allow the passage of solutes improves as the coefficient of permeability increases (Mustabsyirah et al., 2022).

Based on Figure 3(a), it can be observed that the highest permeability value is found in M4 with a 7% additive concentration, amounting to 58.8 L/m^2.hour.bar, an increase higher than other PVDF membranes. This is because the additive added to the dope solution enhances the hydrophilicity of the membrane, thereby improving the membrane's interaction with water. The PVDF/ZIF-8/NMP membrane with a 7% gypsum additive concentration is also believed to have larger pores on the surface, making it easier for solutes to pass through the membrane surface, resulting in higher permeability values and flux (Arahman et al., 2019).

According to Mustabsyirah et al (2022), the rejection coefficient is a value representing the concentration of solutes retained on the surface and pores of the membrane, making it unable to pass through the membrane. The rejection coefficient can be determined using a visible spectrophotometer instrument on the sample solution to be tested.

Based on Figure 3(b), it is found that the PVDF/NMP membrane has high rejection. The highest rejection coefficient is obtained in the membrane without additive addition, with a rejection coefficient value of 70.48%. It is suspected that the morphology of unmodified M6 has a higher density arrangement of pores than the PVDF/NMP membrane with 3%, 5%, and 7% additive additions. This causes BSA to be retained on the membrane surface, enhancing the separation process as the permeate exiting has a lower concentration than the incoming feed. However, in the membrane with a 7% additive concentration (M4), there is a decrease in the rejection coefficient value to 34.21%, caused by the additive altering the membrane's hydrophobic nature to hydrophilic. This change in hydrophilic properties causes the membrane to attract water and leave particles on its surface (Arahman et al., 2019).

Effect of Modification on Stability and Durability

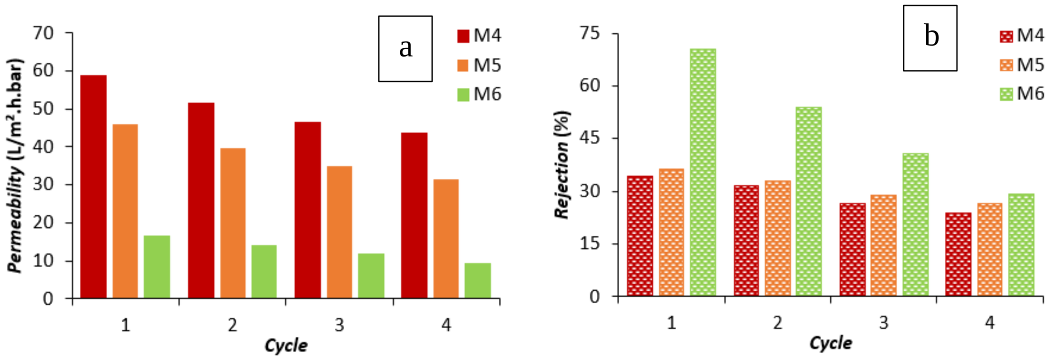


Figure 4. Cyclic separation (a) Pure water permeability and (b) methylene blue rejection

The analysis of changes in water flux and the rejection of methylene blue (MB) through multiple filtration cycles is a crucial aspect of this research. As seen in Figure 4, there is a significant decrease in pure water flux after four cycles of MB separation on the membrane modified with 7% gypsum (M4), decreasing from 58.8 L/m^2.hour.bar to 43.7 L/m^2.hour.bar. A similar trend is observed in M5, containing gypsum and GA crosslinking, where the flux decreases from 45.9 L/m^2.hour.bar to 31.4 L/m^2.hour.bar. Furthermore, the pure PVDF membrane flux (M6) also shows a decline, changing from 16.5 L/m^2.hour.bar to 9.3 L/m^2.hour.bar. The water flux exhibits a continuous decrease with the progression of cycles, reaching the 4th cycle. This phenomenon occurs due to the accumulation of impurity molecules on the membrane surface. Additionally, the development of concentration polarization (CP) layers on the membrane surface is a significant factor contributing to the observed decrease in permeate flux (Du et al., 2019).

Meanwhile, the highest rejection coefficient is observed in the membrane without additive addition, indicated by membrane M6, when compared to other configurations. This is attributed to the more significant retention of MB molecules on the membrane surface, thereby enhancing the efficiency of the separation process. With increased retention, the obtained permeate has a lower concentration compared to the incoming feed, consistent with findings from the study by (Arahman et al., 2019).

When compared to unmodified PVDF membranes, modified membranes exhibit a lower rate of flux reduction throughout the filtration period. Based on findings reported by Rohani et al. (2021), the presence of gypsum in the membrane increases the negative surface charge of the membrane. With a high zeta potential due to the presence of sulfate ions, electrostatic forces are formed between the anion and the membrane surface. Therefore, this phenomenon inhibits the potential fouling on the membrane surface during the filtration process.

Conclusion

Based on the research results, it is concluded that the PVDF/ZIF-8 membrane using gypsum and glutaraldehyde crosslinking as additives has proven to have significant capabilities in reducing dye contaminants in the environment. This conclusion is drawn from a series of experimental tests showing a positive trend in the reduction of dye concentration, with no data or test results indicating significant deviations or variations. In other words, this membrane is effectively capable of reducing the levels of dye pollutants in water or solutions, and the test results are consistent and relevant. This is attributed to the unique characteristics of gypsum, which supports an affinity for water and allows the formation of hydrogen bonds between water molecules and the membrane surface, which has a negative charge in its pores. The data indicates that M4 is the best variable, containing PVDF 11%, ZIF-8 0.3%, and 7% gypsum, resulting in a permeability and rejection of 58.8 L/m^2.hour.barand 34.21%, respectively.

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Author Contributions

Author One modified the membrane, processed data, and wrote the scientific article; Author Two modified the membrane, wrote the scientific article, and conducted MB filtration; Author Three was responsible for analysis and characterization tests on the modified membrane; Author Four was responsible for membrane durability filtration tests; Author Five conducted membrane characterization; The Last Author provided research guidance and finalized the manuscript.

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