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Coagulant bath medium effect towards polylactic acid membranes structure and methylene blue dye removal

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Abstract. The asymmetric polylactic acid (PLA) membrane was prepared via phase inversion method using non-solvent induced separation (NIPS) technique. This study aims to synthesized as well as to characterize the PLA membrane and evaluating the membrane performance on water flux and permeability. In addition, this research also studied the removal performance of methylene blue dye. The polymer solution has been prepared using 12 wt.% of PLA and dissolved in 88 wt.% of Dimethylacetamide (DMAc) as a solvent. Then, the cast film was immersed in different ratio of coagulant bath medium (distilled water: methanol: ethanol) ranging from 100:0:0, 75:25:0, 75:0:25 and 75:12.5:12.5, respectively). Several characterizations were performed which include, membrane contact angle and membrane porosity. Performance PLA membranes were determined in terms of water flux and permeability at 1 bar transmembrane pressure using dead-end permeation cell. Finally, methylene blue (MB) removal efficiency was tested at the same transmembrane pressure. The findings revealed that the increase of alcohol concentration in coagulant bath resulted in higher porosity and lower contact angle. In short, MB dye rejection efficiency is also closely related to the amount of alcohol ratio used in coagulant baths. Increases in concentration of methanol and ethanol in coagulant bath medium increases the membrane porosity thus increased in efficiency of methylene blue rejection.

Keywords: coagulant bath medium; dye removal; non-induced phase separation; polylactic acid membrane

1. Introduction

Wastewater effluents are responsible for a wide range of water contamination problems. Water scarcity, a lack of safe drinking water, and the necessity to treat wastewater before discharging it into the environment have prompted scientists to look for a new low-cost technology that may either replace or improve present wastewater treatment technologies. Wastewater treatment's main purpose is to protect people and the environment by securely disposing of municipal wastewater

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generated during water consumption. In modern places around the world, one of the purposes of wastewater treatment is to use wastewater for irrigation and to preserve groundwater supplies (Edokpayi *et al*. 2017).

Wastewater from the textile and paint industries is a major polluter in our environment. This is because both industries produced unwanted dye wastewater. Both industries produced dye effluent with high levels of colour, pH, suspended solids, chemical oxygen demand, and biochemical oxygen demand. Biological and chemical risks are both related with the use of raw wastewater, particularly in the textile and paint industries. Wastewater may contain bacteria, helminths, protozoa, and viruses, putting it at danger of biological contamination. Furthermore, wastewater which contain high concentration of dyes may contain hazardous substances such as heavy metals, hydrocarbons, and pesticides, and it is subject to chemical danger (Yaseen 2019).

Dyes are compounds that, when applied to a material, temporarily modify the crystal structure of coloured substances to produce a colour. Textiles, pharmaceuticals, food, cosmetics, plastics, photography, and paper are just a few of the industries that use chemicals with a lot of colour. The textile industry in Malaysia produced the most dye wastewater, roughly 200,000 tons per year, accounting for 54% of the total dye effluent. More than half of the dye effluent currently detected in the environment comes from this industry (Drumond *et al.* 2013). Meanwhile, another 21% and 10% of dye effluents are produced by the dyeing and pulp and paper industries. The tannery and paint industries, on the other hand, produce 8% of dye effluents. Finally, the dye manufacturing business generates 7% of dye wastewater. All companies that generate substantial amounts of dye wastewater from various processes (Katheresan *et al.* 2018).

The three most prevalent methods for removing dye from wastewater are biological, chemical, and physical processes. Membrane separation technology is a physical approach that removes between 86.8% and 99% of contaminants. This technology is particularly effective at removing dye from wastewater because of its high efficiency, low cost, simple operation, and lack of sensitivity to harmful compounds (Katheresan *et al.* 2018). Forward osmosis, reverse osmosis, microfiltration, ultrafiltration, and nanofiltration are the many types of membrane technology used in water treatment (Nqombolo *et al.* 2018).

The key to dye removal efficiency using membrane separation technology is the membrane itself. The membrane morphology can be tailored by manipulating the fabrication technique. The most popular and common technique used in membrane fabrication is known as phase inversion. NIPS or known as non-solvent induced phase inversion separation (NIPS) is induced by the exchange of the solvent with the non-solvent from the coagulant bath. By controlling the composition of coagulant bath medium is considered as an effective approach to control the membrane structure formation (Yu *et al.* 2023).

The aim of this work is to study the performance of prepared PLA membrane in methylene blue dye removal by manipulate the coagulant bath medium. The coagulant bath medium was manipulated by combination of distilled water, ethanol and methanol at different ratio.

2. Experimental

2.1 Materials and chemicals

PLA polymer was obtained from Arkema Pte Ltd, Singapore, N, N-dimethylacetamide (DMAc) solvent was acquired from Merck Milipore Corporation, Germany, and Methylene Blue (MB) dye

Table 1 Composition of coagulation bath medium (wt.%)

Membrane	Pure distilled water (wt.%)	Methanol (wt.%)	Ethanol (wt.%)
M1	100	0	0
M2	75	25	0
M3	75	0	25
M4	75	12.5	12.5

was purchased from Sigma-Aldrich, Malaysia. All the chemicals were used as received without any purification except for MB, which was diluted to obtained 0.005 mg/ml stock solution.

2.2 Polymer solution preparation

In a sealed beaker, 12 wt.% of polylactic acid (PLA) polymer and 88 wt.% Dimethylacetamide (DMAc) was mixed using a water bath shaker until a clear solution was obtained. A continuous rotation at 60 rpm was applied throughout the mixing process and the temperature of polymer solution was maintained at 70°C. Then, the homogenous polymer solution was degassed at room temperature until a clear solution was obtained.

2.3 Phase inversion method

Non-solvent phase separation (NIPS) technique was used for the preparation of a flat sheet PLA membrane. Using a hand-casting knife with a gap set at 750 µm, a homogeneous polymer solution was casted onto a glass plate, then exposed to surrounding air for 30 seconds. This stage is known as the evaporation period because it enables some of the solvent to evaporate. Then, the casted film with the glass plate was immersed in a coagulation bath medium for 24 hours. Finally, the solidified membrane was removed from the coagulation water and dried for 24 hours at room temperature (Nasib *et al.* 2017). A specified ratio of distilled water, methanol and ethanol that were used for coagulation baths is tabulated in Table 1.

2.4 Membrane characterization

2.4.1 Porosity

The gravimetric method was used to determine porosity of the membrane. The porosity was measured by soaking the membrane into isopropyl alcohol for 10 minutes and then the membrane surface was dried by filter paper. The membrane was weighed before and after absorption of the isopropyl alcohol. The porosity was calculated using Eq. (1).

$$\varepsilon\,(\%) = \frac{W_1 - W_2/\rho_1}{(W_1 - W_2/\rho_1) + (W_2/\rho_2)} \times 100 \qquad (1)$$

Where ε represents the membrane porosity (%), W_1 and W_2 are wet and dry membrane weights (g), respectively. While ρ_1 is density of isopropyl alcohol (g/cm^3) and ρ_2 is the density of PLA polymer (g/cm^3).

2.4.2 Water contact angle

The contact angle of prepared PLA membranes was determined using the sessile drop method on the membrane surface with distilled water. Images of droplets were captured immediately after liquid deposition on top of the membrane surface using a camera with a 20x Macro zoom lens. The contact angle images were then measured using Image-J software. Each film was evaluated at five different locations, with the average of the results used as the final value (Buahom 2018).

2.5 Membrane performance

A dead-end permeation cell developed by Sterlitech, USA-HP4750 Stirred Cell, a high-pressure chemical resistant stirring cell capable of performing a wide range of membrane separations. It was used to analyzed microfiltration efficiency in terms of water flux and dye rejection of prepared PVDF-co-PTFE membranes. The methylene blue dye was utilized for feed concentrations at 1 bar transmembrane pressures. The membrane module's area in a thin sheet was 1.46 cm^2.

2.5.1 Water flux and permeability

Water flux and permeability was measured by using Eq. (2) and Eq. (3), respectively.

$$J = \frac{V}{A\Delta t} \qquad (2)$$

$$P = \frac{J}{\Delta p} \qquad (3)$$

Where J is permeated flux (L/m^2.h), V is permeated volume of water (m^3), A is area of membrane (m^2), Δt is operating time (h), P is permeability (L/m^2.h.bar), and Δp is the difference in transmembrane pressure (bar).

2.5.2 Methylene blue dye removal

Dye removal test was carried out at the transmembrane pressure of 1 bar for 50 ppm of methylene blue dye solution using a dead-end permeation cell. The concentration of the dye removal after of filtration was measured by using the absorbance tested in UV-Vis. The final dye concentration (C_e) was determined and the dye removal (%) was calculated using Eq. (4) where C_i is initial dye concentrations and C_e is final (equilibrium) dye concentration (mg/L).

$$Dye\ removal\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (4)$$

3. Results and discussion

3.1 Membrane porosity

The porosity of a membrane refers to the amount of empty space within it, and an increase in porosity can directly affect the membrane performance. The porosity of each membrane was calculated using Eq. (1) and they are reported in Fig. 1. The difference can be explained by the variation composition of coagulation bath. In nonsolvent-induced phase separation (NIPS) technique, solidification rate of membrane in coagulant bath is affected by the type of coagulant used in coagulation bath. Distilled water is known as harsh coagulant, meanwhile alcohol like methanol and ethanol are fall in soft coagulant category. 'Harsh' coagulant will lead to fast

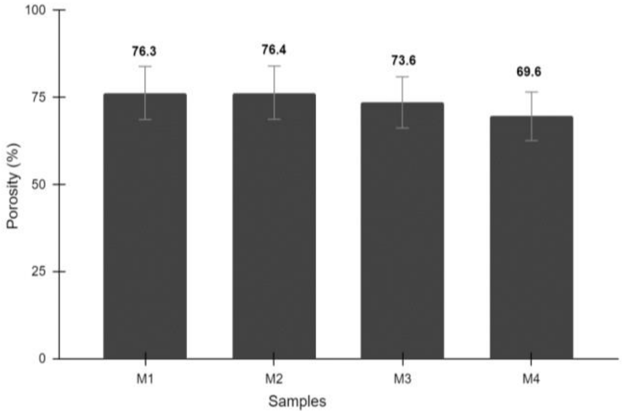

Fig. 1 Polylactic acid membrane porosity at different alcohol ratio in a coagulant bath

precipitation rate and soft coagulant will lead to slower precipitation rate. From Fig. 1, the average porosity of membrane was decreased with the increase of methanol and ethanol concentration. The porosity of M2 membrane prepared with additional of 25% methanol into coagulation bath was recorded higher at 76.4%, as compared to sample M3 (73.6%), which used 25% ethanol. The presence of ethanol (two carbon chemical chain) in the coagulation bath for M3 membrane cause a slower liquid-liquid de-mixing during membrane solidification, hence lead to lower porosity compared to M2 membrane, which using methanol (single carbon) at same percent. However, insignificant different can be seen when compared with sample M1 (100% distilled water as coagulant bath medium). Additional 25% of methanol (single bond carbon) in coagulant bath does not give significant difference in terms of membrane porosity. On the other hand, the lowest porosity recorded was 69.6% which belongs to membrane M4 (12.5% methanol and 12.5% ethanol). This can be explained by further slower liquid-liquid demixing rate as the coagulant bath medium consist of 50% alcohol. Therefore, mixing both ethanol and methanol does not improved the membrane porosity but reducing it.

Results shows in this research is contradict with research done by Tang *et al.* (2019) whereby when ethanol ratio in coagulation bath increases from 0 to 30%, the porosity increases significantly from 1.47 to 13.57%. The addition of alcohol to the coagulant bath lowered the interdiffusion rate of solvent and non-solvent in the phase inversion process thus encouraging more macropore development. In short, as the concentration of alcohol increased, more macropores developed and the porosity decreased. As longer chain alcohol presence in high concentration the coagulant bath, it may cause the membrane to become less porous, whereby a larger pore, or "macrospores" favor to develop, which occur through a process called dissolution-precipitation in coagulant bath.

3.2 Membrane surface hydrophilicity

In water filtration a membrane with more hydrophilic properties is generally preferred because it allows water to pass through more easily while retaining contaminants and impurities. This is because the hydrophilic properties of the membrane create a strong affinity for water molecules, allowing them to pass through the membrane. At the same time, contaminants and impurities that are not as strongly attracted to the water molecules are less likely to pass through the membrane and are instead retained on the surface or within the pores of the membrane. Hence, high water flux and

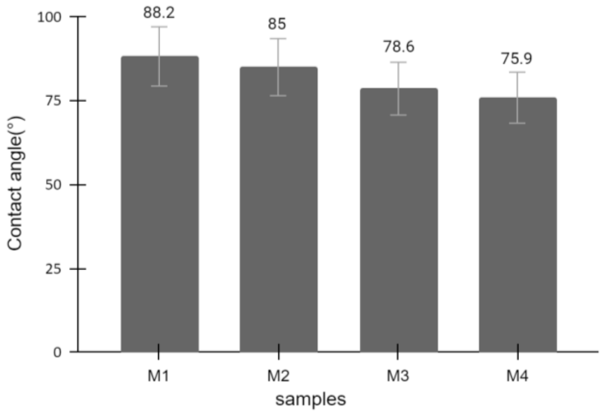

Fig. 2 Polylactic acid membrane contact angle at different alcohol ratio in a coagulant bath

permeability can be obtained (Hegab and Zou 2015). Fig. 2 shows the contact angle of PLA membrane at different ratio of alcohol (methanol and ethanol) in coagulant bath. The contact angle exhibits an overall decrease as the ratio of alcohol increases from 0 to 25%. The highest contact angle recorded at 88.2° was membrane M1 when 100% of distilled water was used. The result indicates the M1 membrane is weak hydrophilic. The lowest contact angle recorded was 75.9° which belongs to membrane M4 where 50% alcohol were mixed with distilled water in coagulant bath, showed that the M4 membrane is highly hydrophilic as compared to other samples. Therefore, it can be concluded that, as the alcohol concentration increases, a slightly improvement of membrane surface hydrophilicity can be obtained.

The patterns are similar to those found in research by Tang *et al.* (2019). Whereby, four samples were prepared by immersing in coagulant baths with various ethanol and distilled water ratio, ranging from 0:100 to 20:80 to 30:70. The recorded contact angle results were 38.25°, 37.4°, 34.3°, and 38.4°, respectively. As the concentration of ethanol in the coagulant bath increased, the contact angle result indicated an overall decrease. According to the study, the above observation happens because of the membrane wetting increased as the ethanol concentration in the coagulant bath increased due to an increase in surface roughness, exhibiting high membrane hydrophilicity.

3.3 Performance of polylactic acid membranes

3.3.1 Water flux and permeability

Water permeability and water flux were performed via dead-end stirred cells. The test was carried out at 1 bar transmembrane pressure. Water flux of membranes is described as the amount of permeate produced per unit area of membrane surface per time. Meanwhile, water permeability is defined as the amount of permeate flux produced per transmembrane pressure. Fig. 3 illustrates the trends of pure water flux of prepared polylactic acid membranes.

From Fig. 3, the pure water flux shows an overall increase as the alcohol concentration increases. At 1 bar transmembrane pressure, the highest water flux recorded was 3281.9 L/m^{2}h which belong to membrane M4 (12.5% methanol and 12.5% ethanol) while the lowest water flux recorded was 1783.3 L/m^2.h belong to membrane M1 (0% alcohol). This can be explained by membrane hydrophilicity. This is due to increasing the alcohol content in the coagulant bath, increased membrane hydrophilicity, which attracts the passage of water molecules through the membrane

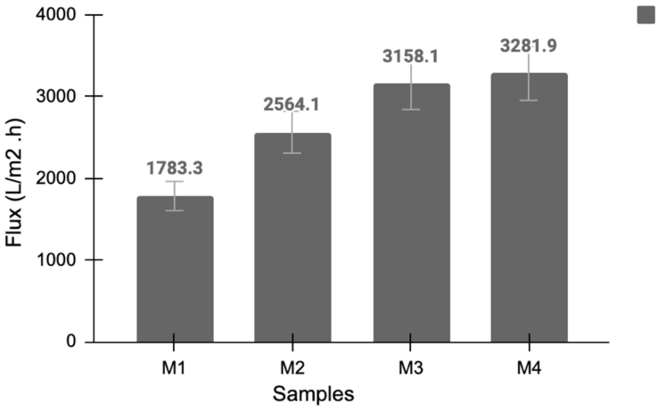

Fig. 3 Polylactic acid membrane water flux at different ratio of alcohol in coagulant bath

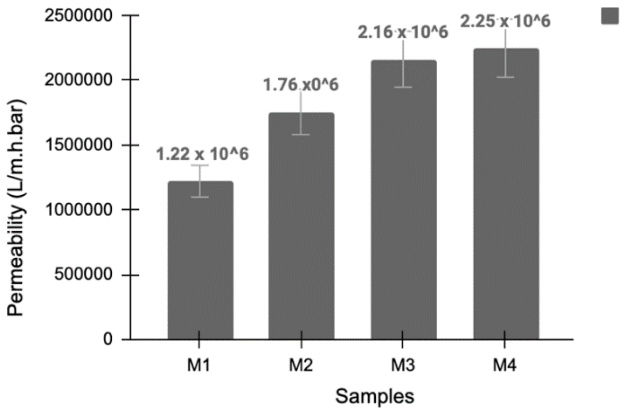

Fig. 4 Polylactic acid membrane permeability at different ratio of alcohol in coagulant bath

matrix and enhances their permeability of pure water flux.

Meanwhile, Fig. 4 illustrated the water permeability of prepared polylactic acid membrane at 1 bar transmembrane pressure. The highest water permeability recorded was 2.25×106 L/m^2.h.bar which belongs to membrane M4 (12.5% methanol and 12.5% ethanol) while the lowest water permeability recorded was 1.22×106 L/m^2.h.bar belongs to membrane M1 (100% distilled water). According to Thürmer *et al.* (2012), increased alcohol concentration in coagulant bath increased hydrophilicity of membranes thus increased the water permeability. To support the statement above in a material with high permeability, the pore spaces are interconnected, allowing water to move from one to the next; in a material with low permeability, the pore spaces are isolated, trapping the water inside (Hommel *et al.* 2018).

3.3.2 Methylene blue dye separations

The PLA membrane separation performance on dye rejection performance was carried out using methylene blue dye. Methylene blue dye solutions were prepared in concentration of 0.005 mg/ml and the test was carried out via dead-end stirred cell at 1 bar of transmembrane pressure. Fig. 5 shows the percentage of methylene blue dye rejection of prepared Polylactic acid (PLA) membrane.

From Fig. 5, the percentage of dye rejection shows slightly increasing as the ratio of alcohol

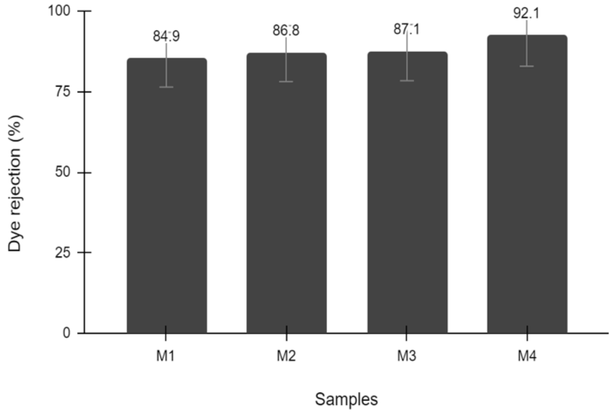

Fig. 5 Polylactic acid membrane permeability at different ratio of alcohol in coagulant bath

increased from 0 to 25%. The highest percentage of dye rejection recorded is membrane M4 which 92.1% which used mixture of 12.5% of methanol, 12.5% of ethanol and distilled water in coagulation bath. The lowest dye rejection recorded was 84.9% which belong to membrane M1 (100% distilled water). From the findings, as the alcohol concentration in coagulant bath increased, the percentage of dye rejection increased despite the low porosity value obtain. This means that the membrane can effectively filter out and reject a high percentage of dye particles. This indicates that the membrane can effectively block and filter out unwanted particles, while still allowing necessary substances to pass through (Nikooe and Saljoughi 2017).

According to Van Tran *et al.* (2019), MB dye is positively charged due to quaternary ammonium cation and had a positive zeta potential of +8.5mV. Meanwhile, the zeta potential of PLA membrane is about -23mV (Zhu *et al.* 2015). The MB dye was separated via electrostatic attraction forces, whereby the MB dye molecules adhered to the PLA membrane surface and the filtered water pass through the membrane. However, different percentage of dye removal performance among the samples can be explained due to the membrane hydrophilic properties. As discussed in Section 3.1, M4 membrane possess the lowest contact angle at 75.9°, which has the most hydrophilic properties among other samples. The hydrophilic property of the membrane allows more water to permeate through and retain MB dye behind, hence the highest dye rejection is obtained.

4. Conclusions

Coagulant bath medium in NIPS technique has been manipulated in this study by using different compositions of distilled water, ethanol, and methanol. In conclusion, the combination of ethanol and methanol at the same ratio and distilled water can produce the most hydrophilic membrane properties. Due to better hydrophilic properties, the PLA membrane can give high water flux and permeability and finally, the highest MB dye rejection can be obtained.

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