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Modification of polyetersulfone (PES) membrane by using jernang (*daemonorops draco blume*) as a natural additive on humic acid fouling

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Abstract. This paper reports on the effect of adding Jernang additives on the performance of PES membranes. The membrane was made by mixing PES 16.5%, Jernang 1%, and NMP 82.5%, using the Non-solvent Induced Phase Separation (NIPS) method. The chemical group of Jernang has been studied in this paper. The addition of Jernang additives has succeeded in improving the performance of PES membranes. Pure water flux increases to 18.77 LMH from the initial flux of 1.66 LMH. Humic acid removal showed reasonable results up to 77.52%. Moreover, this membrane has good antifouling properties, but less stable under strong acid and alkaline solution.

1. Introduction

Global water crisis is the biggest problem in the 21st century, especially in developing countries. Although water is a renewable source, only 1% of 3% of fresh water can be used by humans for consumption (97% is sea water). According to many experts even 1% is sufficient because the supply of fresh water is not limited through the pure water cycle, but its availability is not evenly distributed around the world [1]. Various water treatment methods are used to reduce contaminants in water, including coagulation-sedimentation [2], disinfectants [3], chemical oxidation [4], and aerobic and anaerobic digestion processes [5]. Among these methods, membrane technology has attracted many researchers and industrial sectors because of several advantages, including low energy consumption, simple operation process, easy to combine with other processes, optimizing membrane performance, and does not require a large area [6].

Polyethersulfone (PES) is the polymer most often used for ultrafiltration membranes. This is due to the PES has good thermal, chemical resistance and mechanical strength. However, this polymer is hydrophobic, which causes membrane fouling easily when applied to water treatment. Fouling can cause a decrease in membrane performance; therefore, modification of the membrane surface is important to produce a membrane that has anti-fouling properties [7]. The most effective modification is by adding additives to the polymer solution. This modification not only increases the hydrophilicity of the membrane, but is also useful for changing the interaction between microparticles and the membrane



surface [8]. There have been many additives used in membrane modification. Generally obtained from chemicals which are relatively expensive. Therefore, several researchers have developed additives from nature and have done it successfully. Various natural additives that have been used include nanosilica from rice husk and sugarcane bagasse [9], nanocarbon from palm shell waste [10], and activated carbon from *Jatropha* seed shell [11]. Besides these additives, there is a natural additive that has never been studied before, that is Jernang.

Jernang or globally known as dragon's blood is the result of red rattan secretions. Dragon's blood is generally used for all types of resins obtained from four genus, including *Croton* (*Euphorbiaceae*), *Dracaena* (*Dracaenaceae*), *Daemonorops* (*Palmaceae*), and *Precaurus* (*Fabaceae*). The type of dragon's blood that grows in Indonesia comes from the genus *Daemonorops* spp., which is known by residents as jernang. Previous studies have reported that this resin contains terpenoids, flavonoids, phenols and dracorodine [12]. The amount of flavonoid content varies depending on the type of jernang and its quality. Flavonoids can increase the hydrophilicity of the membrane by substituting a hydroxyl group (-OH) into the polymer structure [13]. This research will use jernang from Aceh (*Daemonorops dracoblume*) as an additive. This research studied the effect of adding additives to the performance of PES membranes. These experiments include filtration tests, humic acid rejection, antifouling and membrane stability.

2. Experimental

2.1. Material

Polyethersulfone (PES, Ultrason E6020P) used as the main polymer which was purchased from BASF Co. (Ludwigshafen, Germany). 1-N-methyl-2-Pyrrolidone (NMP, 99.5%) used as the polymer solvent which was purchased from Merck (Hohenbrunn, Germany). Jernang (*Daemonorops draco Blume*) used as the membrane additive which was obtained from farmers in Central Aceh. Humic acid (sodium salt, technical grade 50-60%) purchased from Sigma-Aldrich which was used as the model organic foulant to test the rejection and antifouling ability membrane.

2.2. Preparation and characterization of Jernang

Jernang was minimized using a mortar and pestle until powdery. Then the Jernang powder was filtered using a 180 μm sieve. This characterization consists of analyzing the Jernang functional groups using Fourier Transform Infrared (FTIR). FTIR spectra were analyzed by Shimadzu Prestige FT-IR 6400 in the range 4000 cm^{-1} to 400 cm^{-1} at room temperature. Before analysis, Jernang was mixed with KBr with a ratio of 1: 9 (Jernang: KBr).

2.3. Membrane fabrication

In this study two flat sheet membranes were fabricated. The first membrane (M0) was composed of 17.5% PES and 82.5% NMP. Then the second membrane (M1) was composed of PES 16.5%, Jernang 1%, and NMP 82.5%. The membrane was produced using the Non-solvent Induced Phase Separation (NIPS) method. Dope solution was made by dissolving PES and Jernang into NMP for 24 hours until homogeneous. Then leave for 6 hours at room temperature until the air bubbles completely disappear. Each dope solution was molded onto a lip at room temperature using an automatic applicator (YBA-3, Japan) with a thickness of 300 μm . Then the lip was dipped into a bath containing non-solvent distilled water, during the immersion process a thin layer will be formed which is separated from the lips. Finally, the membrane was washed and stored as shown in Figure 1.

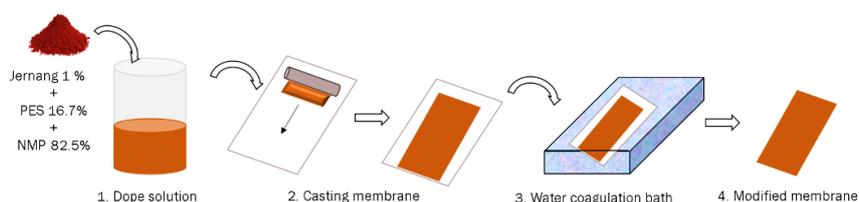


Figure 1. Illustration of membrane fabrication.

2.4 Evaluation of permeation and separation performance

Membrane permeation was evaluated by filtering the membrane with distilled water. The membrane was filtered at a trans membrane pressure of 3 bar. This test is useful for knowing how much permeate rate can be obtained. The dead-end module was used with a batch system as Figure 2 portrays. Permeate was collected in a beaker and its total weight was recorded every 10 minutes until the permeate weight was constant. Pure water flux was calculated using Equation 1

$$J = \frac{Q}{A \cdot t} \quad (1)$$

Where J is the flux of pure water (L/m².h), Q is the permeate volume (L). t is the filtration time (hours), and A is the membrane surface area, which in this study was 5,667x10⁻⁴m². Separation performance was evaluated by filtering the membrane with an artificial solution of humus acid with an initial concentration of 50 ppm. The permeate concentration was analyzed using a UV-VIS spectrometer. The rejection coefficient (R) was calculated using equation 2.

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (2)$$

Where R is the rejection coefficient (%), C_f is the feed concentration (mg/L), C_p is the permeate concentration (mg/L).

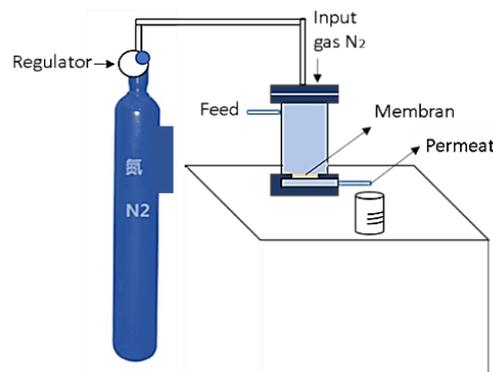


Figure 2. Set up filtration process.

2.5. Antifouling performance assessment

The antifouling test was useful for studying the resistance of membranes to fouling. This test was carried out in several stages, referring to the research of Jiang et al, 2014 [19]. The membrane was filtered with distilled water to obtain the initial pure water flux (J_{w1}). Then the membrane was filtered with humus acid solution (J_{HA}). After that, the membrane was washed using the backwash technique for 10 minutes with a pressure of 0.5 bar. In the final stage, the cleaned membrane was re-filtered with distilled water (J_{w2}). Data from this entire test series can be used to calculate the quantity of water flux that can be recovered after backwash, which is commonly known as flux ratio recovery (FRR). FRR can be calculated using Equation 3.

$$FRR = \frac{J_{w1}}{J_{w2}} \times 100\% \quad (3)$$

Besides FRR, the membrane fouling behavior can also be studied from the flux loss caused by total fouling. Total fouling (R_t) is a combination of reversible (R_r) and irreversible (R_{ir}) fouling. These three behaviors are expressed mathematically in Equation 4 – 6.

$$R_T = \frac{J_{W1} - J_{HA}}{J_{W1}} \times 100\% \quad (4)$$

$$R_r = \frac{J_{W2} - J_{HA}}{J_{W1}} \times 100\% \quad (5)$$

$$R_{ir} = \frac{J_{W1} - J_{HA}}{J_{W1}} \times 100\% \quad (6)$$

2.6. Membrane stability test

This test is to study the stability of the membrane when used in strong alkaline or strong acid feed conditions. This test was carried out by immersing the membrane in 1 N HCl solution (pH: 1) and 1 N NaOH (pH: 14) for a week. Then the membrane was re-tested for pure water flux and compared with its initial flux, so that the stability of the membrane could be evaluated.

3. Result and discussion

3.1. FTIR characterization of Jernang

FTIR analysis was carried out to identify chemical groups in Jernang. The FTIR spectrum is presented in Figure 3. The results of this analysis show a similar trend to the study reported by Nunes et al [15]. There are a dominant chemical group in Jernang, including the wave number 3267 cm^{-1} O-H stretch, 2846; 2939; 2999 cm^{-1} C-H stretch alkanes, 1730 cm^{-1} C = O stretch, 1602; 1647; 1500 cm^{-1} N-H bend, 1423; 1448; 1500 cm^{-1} C-C aromatic, and 1112 cm^{-1} C-N aliphatic amines.

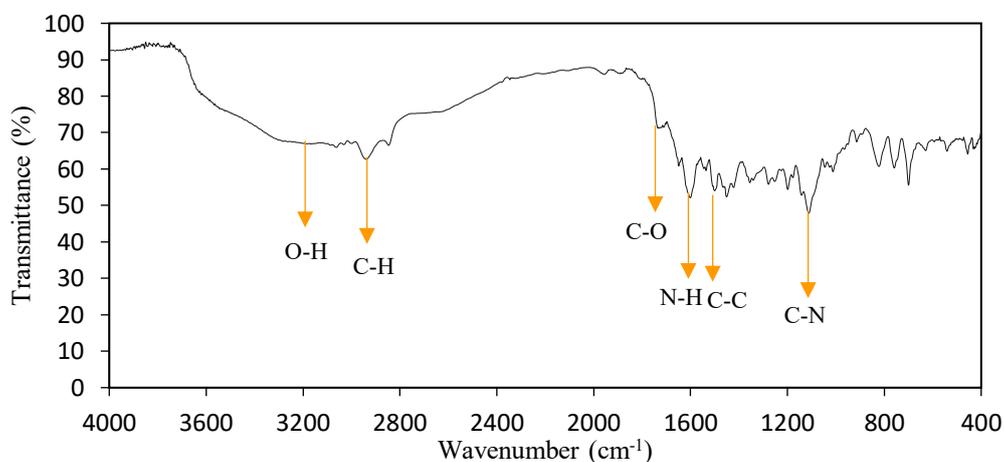


Figure 3. FTIR spectrum of Jernang.

3.2. Pure water flux

Figure 4.a shows that the addition of 1% Jernang to the PES membrane can increase the pure water flux up to 11 times greater than the pure PES membrane, which is 18.77 LMH. This proves that Jernang can increase the hydrophilicity of PES membranes. The hydrophilicity of a membrane increased the flux of pure water because it can reduce hydraulic resistance and increase pore size and membrane porosity [9].

3.3. Humic acid removal

In Figure 4.b humic acid flux shows the same tendency as the pure water flux, the difference in the amount of permeate. The humic acid flux is less than the pure water flux due to concentration polarization throughout the filtration time. Based on Figure 4, it can be seen that the addition of 1% Jernang causes rejection to decrease by 3.77% percent of the pure PES membrane. This is because the pore size and porosity of the membrane are increased which allows more foulant to be released during filtration.

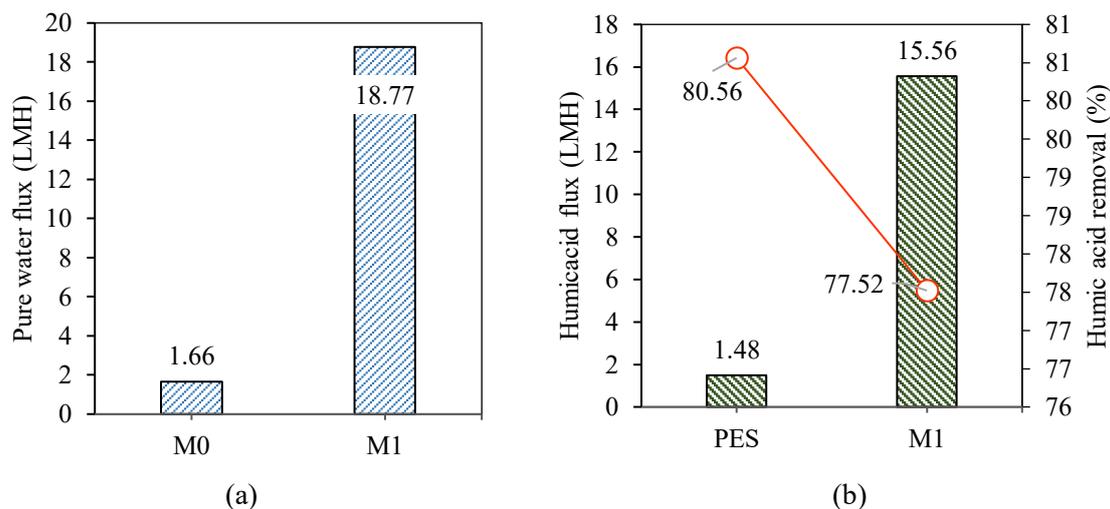


Figure 4. (a) Effect of Jernang additive on pure water flux, (b) Effect of adding jernang additives on humic acid removal.

3.4. Anti-fouling performance

Fouling is caused by deposits of organic impurities on the surface or inside the pores of the membrane. Membrane fouling can be reversible and irreversible. The concentration polarization is reversible, so it can be solved by backwashing. However, in irreversible fouling, the foulant is in the pore of the membrane which causes pore constriction, so at this stage the foulant cannot be physically removed [14]. The effect of impurities on the membrane can be observed from the performance of the membrane, which is shown by the loss of flux during the filtration process, as in Figure 5.a.

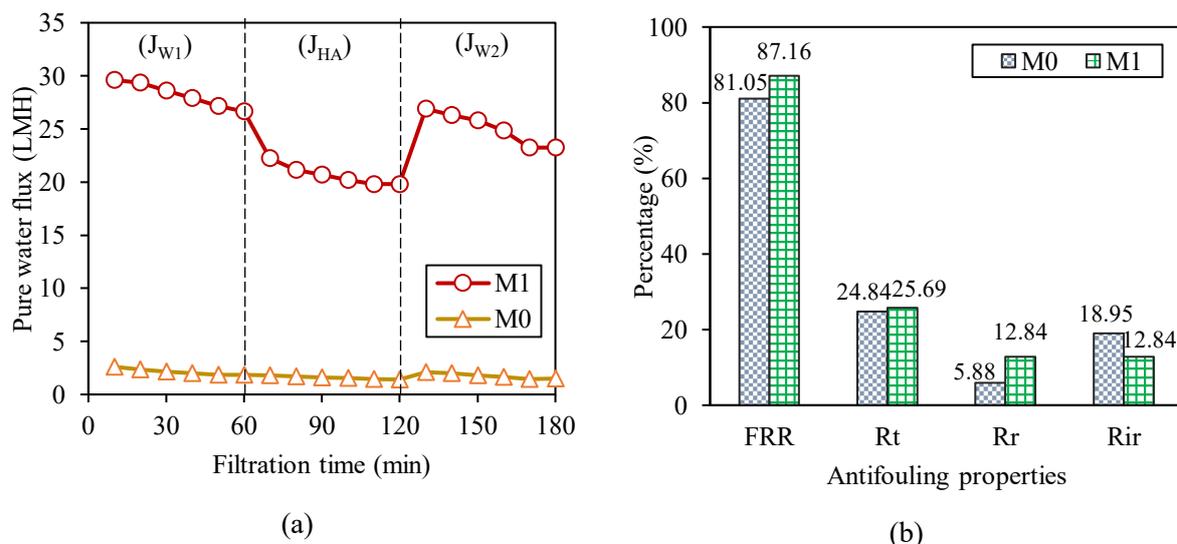


Figure 5. (a) Reduction of flux and membrane recovery profiles during filtration with water and humic acid solution, (b) anti-fouling performance of pure PES membrane and PES + Jernang 1%.

This whole series of processes is carried out in order to measure the quantity of water flux that can be recovered after backwash, which is commonly known as flux ratio recovery (FRR). Apart from FRR, the fouling behavior can also be studied from the flux loss due to total fouling, reversible, and irreversible, which are summarized in Figure 5.b The results of the anti-fouling study showed that adding 1% Jernang to PES membrane solution increased the antifouling properties of the membrane. This was

indicated by the FRR value on the M1 membrane reaching 87.16% and irreversible fouling of 12.84%. The test results prove that this modification is able to produce a membrane that has excellent fouling resistance.

3.5. Stability of membranes

The results of pure water flux testing before and after immersion can be seen in Figures 6. The immersion of the membrane in strong acids and alkaline solution increases the pure water flux of the modified PES membrane (M1). The flux increases 3 times more than the initial flux before the membrane is immersed. This significant value indicates that the PES membrane with added 1% Jernang is not stable against strong acid and alkaline conditions. Besides, the neat PES (M0) presents a great result. The pure water flux after immersion in strong acids and alkaline shows an amount similar to the initial flux. So, it can be concluded that neat PES has very good chemical stability.

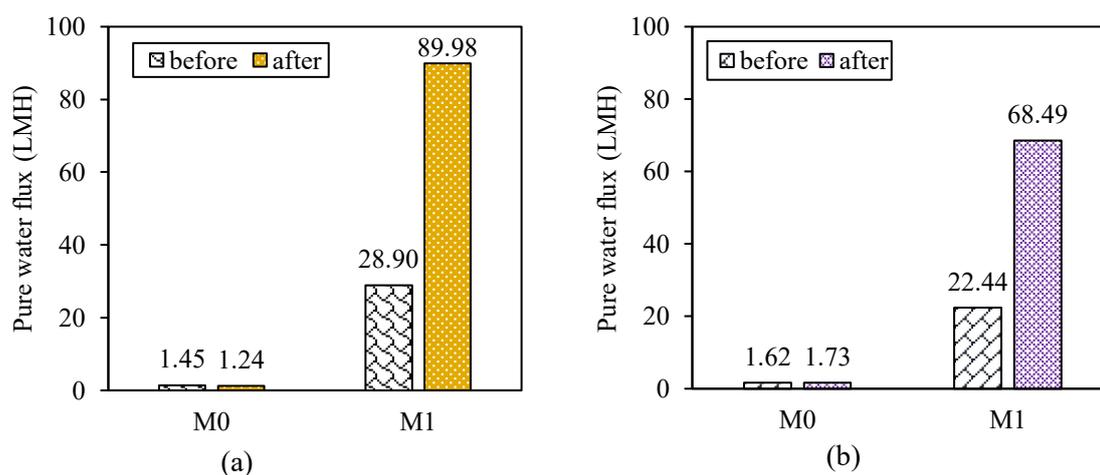


Figure 6. Flux before and after immersing the membrane in (a) strong acid solution and (b) strong alkaline solution.

4. Conclusion

The conclusion of this research is that modification of PES membrane with the addition of 1% jernang additive has been able to increase the hydrophilicity of the membrane followed by an increase in pure water flux. Humic acid removal showed reasonable results up to 77.52% and this membrane has good antifouling properties. However, PES membrane modification causes the membrane to be unstable under strong acid and alkaline conditions. It is necessary to learn more about the characteristics of this membrane and the effect of Jernang concentration on the performance of PES membranes.

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