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ORIGINAL RESEARCH

FABRICATION AND CHARACTERIZATION OF POLYETHERSULFONE (PES) MEMBRANES BY BLENDING POLYMERS FOR REMOVAL OF ORGANIC COMPOUNDS IN AIR

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ABSTRACT: *The PES membrane was modified using a polymer blending method to improve the performance and characteristics of the membrane. This research aims to see the effect of adding biosilica additives on the performance characteristics of PES membranes and determine the optimal composition of additives and solvents for making membranes. The membrane was made using the Non-solvent Induced Phase Separation (NIPS) method with a composition consisting of 18% PES, with the addition of varying concentrations of silica (1%, 2%, 3%, and 4%) and the membrane using the solvent N-Methyl- 2 Pyrrolidone (NMP) and Dimethyl Sulfoxide (DMSO). Membrane characterization was carried out by observing membrane morphology using Scanning Electron Microscopy (SEM), membrane surface functional group analysis test using Fourier Tranform Infrared (FTIR), and membrane porosity test using the dry-wet weight procedure method. The highest porosity value was found on membrane B2 using a solvent DMSO with 2% silica at 16.88%. Membrane performance was carried out by pure water flux testing, the highest pure water flux value was found in membrane B2 with 2% silica, namely 64.14 L/m2.h. The antifouling test uses flux ratio recovery, the highest antifouling value was found on the A3 membrane with 3% silica, namely 91.3%. As well as rejection of the humic acid solution as a Natural Organic Matter (NOM) sample model using the ultrafiltration (UF) module with a dead-end filtration flow system, the highest rejection value was found on the B2 membrane with 2% silica, namely 64.4%.*

Keywords: *Antifouling, Polyethersulfone, Silika, blending polimer*

INTRODUCTION

Water pollution is a serious problem that threatens the survival of humans and the environment. One type of pollutant that can threaten human health and the environment is organic compounds found in waste water. Organic compounds in wastewater from industrial waste, agricultural waste and domestic waste. Therefore, an effective wastewater treatment method is needed to remove these organic compounds. The method that can be used is to use a polymer membrane. The advantages of this membrane technology are that there is no need to add chemicals, the energy used is quite low, the process is simple, and environmentally friendly and has high selectivity [1]. The material used in making the membrane is Polyethersulfone (PES). This is because PES has the advantages of good thermal stability, high resistance to heat and chemicals, and good mechanical and membrane-forming properties. However, PES has a weakness, namely that it easily experiences fouling on the surface. Fouling of the membrane will significantly reduce the performance (flux and selectivity) and membrane durability, thereby increasing operation and maintenance costs [2].

The chemical compound SiO2 (silica dioxide) is obtained from nature such as mineral silica, vegetable and crystal

synthesis. Silica is a compound formed through the polymerization of silicic acid, which has a crystalline structure in the form of natural compounds, while silica compounds made synthetically are amorphous. The mineral silica is usually obtained through a mining process. However, because it is difficult to obtain, other alternatives such as vegetable resources and synthesis processes are options for obtaining these silica compounds [3]. One of the advantages that silica has is that it is easily modified with certain chemical compounds. The way to obtain silica from natural materials is by using the extraction method. In this method, two immiscible liquid mixtures are separated. The factors that influence this are temperature, solvent concentration, extraction time, and stirring [4].

The addition of silica additives can be done by blending or directly mixing several additives into the polymer matrix. This blending technique has the advantage of being easy to operate and significantly influencing the membrane characteristics. The addition of silica additives changes the characteristics of the top layer, pore size, thickness, hydrophilicity and membrane structure such as porosity [5], [6].

Polymer blending is a technique of mixing two or more types of polymers to improve the physical and chemical properties of the resulting polymer membrane. In making polymer membranes using the blending technique, the main polymer used is (PES) which has good properties in separating organic compounds from water. Apart from PES, additional materials in the form of other polymers are also used which can improve the quality of the polymer membrane produced [7]. In the field of separation engineering, membrane technology plays a big role, especially in overcoming clean water problems, due to its advantages such as being able to operate with minimum use of chemicals, low energy consumption, environmental friendliness and simple process methods. One of the materials that can be used in making membranes is (PES), which has the advantages of good thermal stability, high resistance to heat and chemicals, and good mechanical and membrane-forming properties.

In making membranes, silica is used as an additive to improve the mechanical and thermal properties of the membrane. Silica is often used as an additional material because it has very strong properties and is resistant to high temperatures. Apart from that, silica can also increase the thermal stability and corrosion resistance of membranes. The addition of silica in making membranes can significantly influence the properties and performance of the membrane. However, the effect of silica addition on membrane properties and performance is also influenced by the silica concentration in the membrane manufacture. If the silica concentration is too low or high, it can reduce the properties and performance of the membrane. Therefore, it is important to determine the appropriate silica concentration to achieve optimal membrane properties and performance [1]

This research aims to determine the optimal composition of additives and solvents for making membranes. As well as studying the effect of adding NMP and DMSO solvents on the characteristics and performance of the resulting PES membrane. Examining the mechanical properties, hydrophilicity and antifouling of the resulting modified membrane.

METHOD

The main ingredients in making membranes include PES Ultrason E6020P with solvents such as N-Methyl-2 Pyrolidone (NMP) and Dimethyl Sulfoxide (DMSO) as well as distilled water as a non-solvent and silica dioxide as an additive. Humic acid (technical grade 50-60%) is used as an artificial solution for membrane rejection tests.

Equipment used in making membranes includes glass bottles, magnetic stirrers, storage containers, coagulation tanks, measuring flasks, beakers, Petri dishes and hot plates. Additionally, glass plates and casting knives are used to print membranes.

Membrane performance will be carried out by testing pure water flux and humus acid rejection using a dead-end filtration membrane module, a tube containing nitrogen gas and a hose.

The membrane solution is made by dissolving PES with silica using NMP and DMSO solvents, the presence of NMP and DMSO solvents breaks down the clumped cellulose structure while helping to produce cellulose with a better structure according to the composition listed in Table 2.1. The solution was stirred until homogeneous on a hotplate for 24 hours. The next stage is that the dope solution is printed on a glass plate using an applicator with a thickness of 200 µm. Then the glass plate is dipped into a coagulation bath containing distilled water. During the dipping process a thin layer will form which separates from the glass plate. The membrane is washed and stored in a container containing distilled water.

Table 2.1 Composition of Dope Solution

Membrane	PES (%)	Biosilica (%)	Solvent (grams)	
			NMP	DMSO
A0	18	0	82	-
A1		1	81	-
A2		2	80	-
A3		3	79	-
A4		4	78	-
B0		0	-	82
B1		1	-	81
B2		2	-	80
B3		3	-	79
B4		4	-	78

Membrane Characterization

Morphology Test

To determine the morphology of a membrane which includes the surface of the membrane and the cross-section of the membrane, Scanning Electron Microscopy (SEM) can be used.

Functional Group Test

Functional group analysis and determining the constituent components of the membrane can be analyzed using Fourier Transform Infrared Spectroscopy (FTIR), to determine the compounds contained in the membrane that influence the membrane characteristics.

Porosity Test

This porosity test is carried out using the dry-wet weight procedure method, this method measures the weight of the membrane in wet and dry conditions. Equation 2.1 is used to calculate membrane porosity.

$$\varepsilon = \frac{\omega w - \omega d}{\rho \, x \, A \, x \, l} \quad \text{x } 100\% \qquad (2.1)$$

Membrane Performance Test

Pure Water Flux Test

The membrane performance test consisted of measuring the permeation flux of pure water using an ultrafiltration (UF) module. The membrane performance testing uses water feed by passing it through the dead-end filtration module. Pure water flux is measured by the volume of permeate over a certain time period until it reaches a constant state. The flux is calculated using Equation 2.2

$$J = \frac{V}{A.t} \qquad (2.2)$$

Rejection/Selectivity Test

Membrane selectivity testing was carried out using a 50 ppm humic acid solution, which was used as a Natural Organic Matter (NOM) model to remove natural organic components in water. Humic acid is inserted into the membrane module, where the concentration of humic permeate (Cp) and retentate (Cf) acids is analyzed using a UV-Vis spectrophotometer. Membrane rejection is calculated using Equation 2.3

$$R = \frac{C_f - C_p}{C_f} \text{ x } 100\% \quad (2.3)$$

Antifouling Properties Test

Membrane antifouling properties can be tested by measuring the Flux Recovery Ratio (FRR), which is an indication of the membrane's ability to restore permeation performance after backwashing using a dead end type ultrafiltration membrane module. The antifouling properties of the membrane are calculated using Equation 2.4

$$FRR = \left(\frac{Jw2}{Jw1}\right) \text{ x } 100\% \quad (2.4)$$

RESULTS AND ANALYSIS

Membrane Characteristics

Membrane Morphology Analysis Using SEM

Morphological analysis of the membrane used a scanning electron microscopy (SEM) type SEM JOEL JSM 6360 LA which consists of a cross-section with a magnification of 2500 times. The results of membrane morphology analysis using the SEM test equipment can be seen in the asymmetric morphology of each membrane in Figure 3.1.

In this SEM image, three layers can be seen, namely the dense, intermediate and buffer layers. The dense layer is the layer that is on the top surface of the membrane. Meanwhile, the intermediate layer is the layer that comes after the dense layer and is then coated with a buffer layer. It can be seen in Figure 3.1 that the structure of the PES membrane with DMSO as a solvent shows a solid structure on the top layer and finger-like pores on the bottom. The structure of the membrane will change when silica is added. In the membrane with the addition of silica, significant changes were seen, where in the bottom layer the pores that formed finger-like macrovoids appeared to be larger in size compared to the membrane without the addition of silica. The PES membrane with NMP solvent shows a membrane structure with a finger-like pore shape with a small size in the top layer, while in the bottom layer it looks macrovoid in size. However, the number of pores in membranes with additives is greater than in membranes without silica additives, this is because the addition of additives can increase the number and size of finger-like pores, thus affecting the morphological structure of the membrane [7].

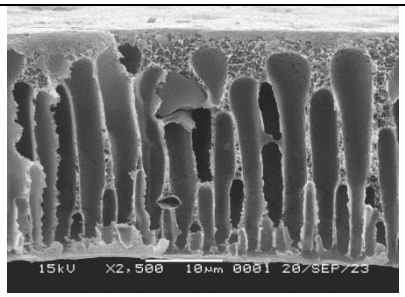
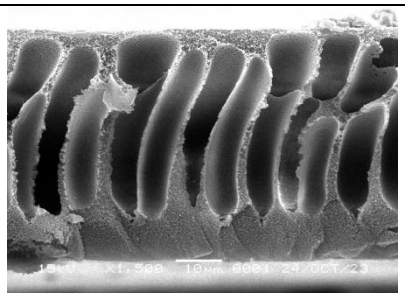
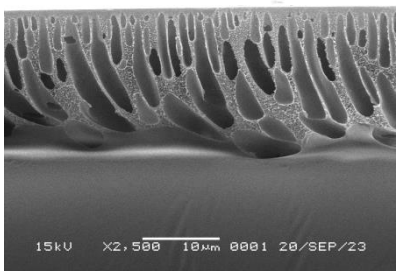
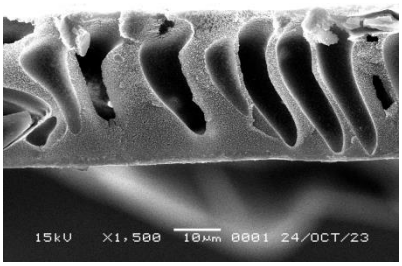
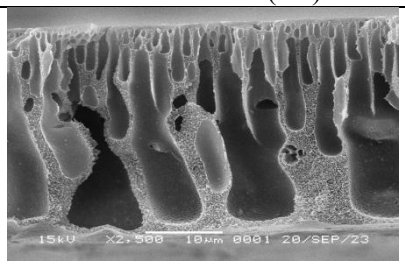
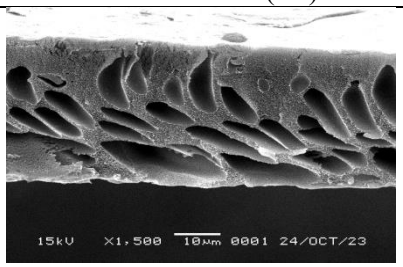
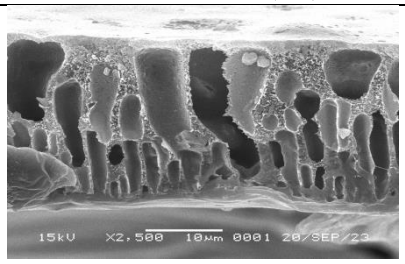
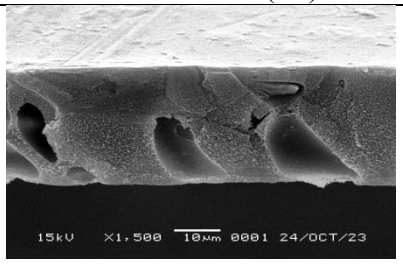
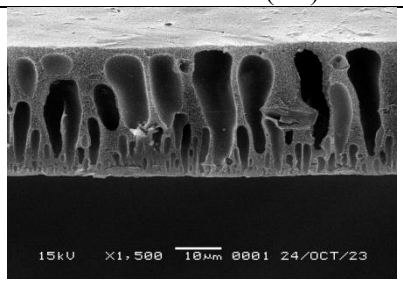
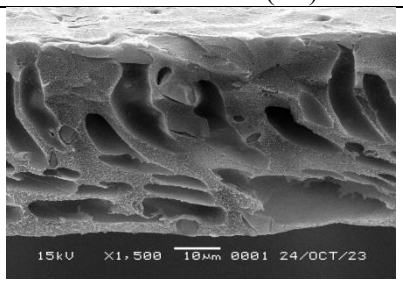
Cross Section	
NMP Solvent	DMSO Solvent
 Without additives (A0)	 Without additives (B0)
 With 1% silica (A1)	 With 1% silica (B1)
 With 2% silica (A2)	 With 2% silica (B2)
 With 3% silica (A3)	 With 3% silica (B3)
 With 4% silica (A4)	 With 4% silica (B4)

Figure 3.1 Morphological structure of the membrane cross section using SEM

Membrane Functional Group Analysis Using FTIR

Functional group analysis is a technique for identifying functional groups in organic compounds. Functional group analysis of a sample is determined by comparing the absorption bands created in the infrared spectrum with the spectrum of a

known reference compound. Functional group analysis was carried out using the Fourier Transform Infrared (FTIR) instrument [8]. The results of FTIR analysis of membranes with NMP and DMSO solvents can be seen in Figure 3.2 and Figure 3.3.

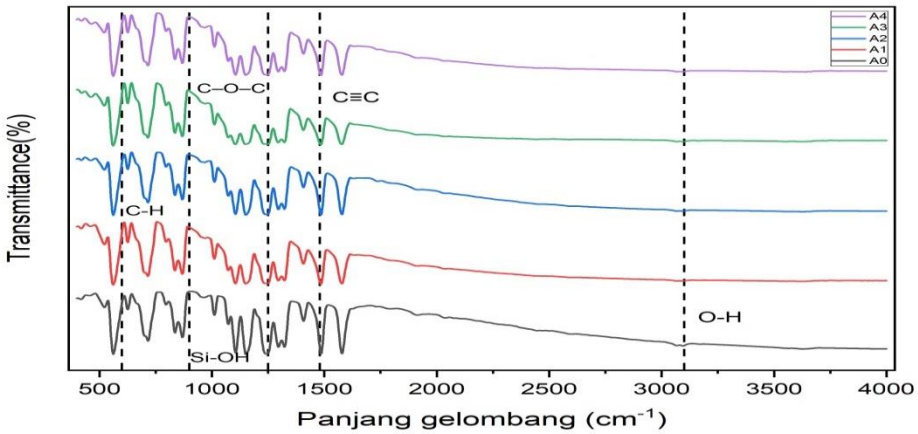


Figure 3.2 FTIR test results on membranes with NMP solvent

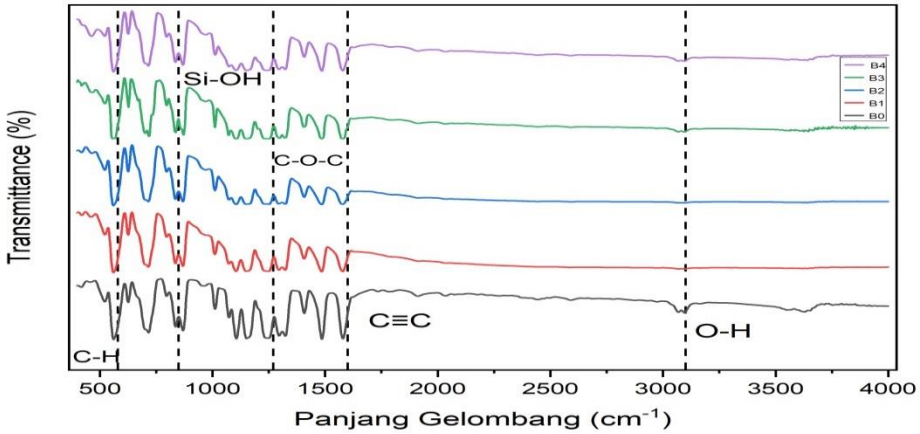


Figure 3.3 FTIR test results on membranes with DMSO solvent

From Figure 3.2 and Figure 3.3 it can be seen that the polyethersulfone (PES) membrane with NMP and DMSO solvents shows the results of FTIR spectrum analysis of the presence of hydroxyl groups (O-H) at a wavelength of 3350-3500 cm-1, aromatic C-H groups at a wavelength of 750-900 cm-1, the (Si-OH) group at a wavelength of 900-1000 cm-1, the aromatic ring group (C≡C) at a wavelength of 1450-1500 cm-1, and the aromatic ether group (C-O-C) at a wavelength of 1230- 1270 cm-1. Based on functional group analysis using FTIR, the prepared polyethersulfone membranes have peaks that are similar to each other. The (Si-OH) group shows the existence of hydrogen bonds between the silanol groups from the silica network and the amine groups or oxy groups on the membrane [8].

Membrane Porosity Analysis

The aim of measuring membrane porosity is to determine the amount of empty space between the materials in the membrane. The results of measuring porosity on polyethersulfone membranes with NMP and DMSO solvents without additives and with the addition of silica additives, with silica concentrations of 1%, 2%, 3% and 4% can be seen in Figure 3.4 below.

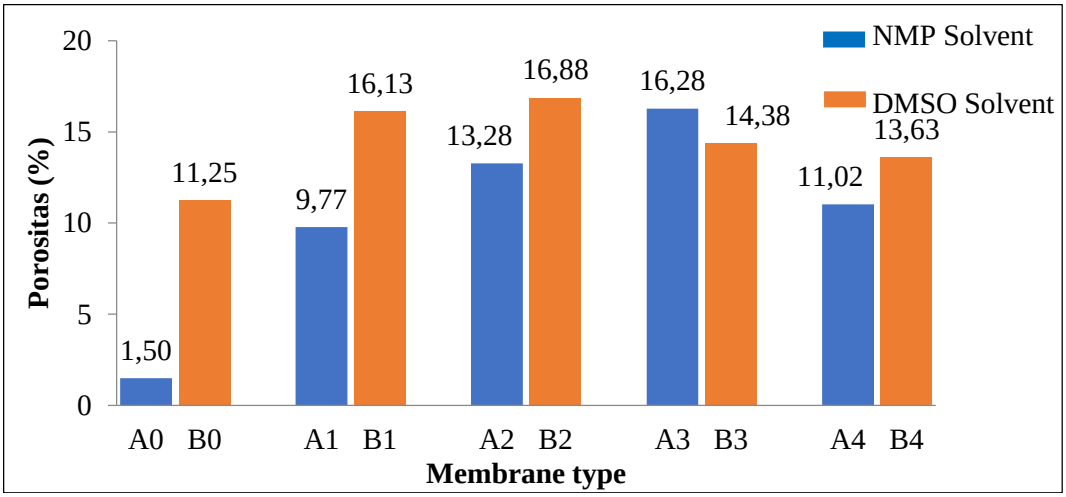


Figure 3.4 Porosity value on the membrane

The presence of hydrophilic (-OH) groups makes the membrane more hydrophilic, so that the phase inversion process in the solvent increases membrane porosity. The modified membrane becomes more porous due to the addition of other materials or other hydroxyl groups, thereby increasing the percentage of membrane porosity. One of the parameters that influences membrane performance is porosity. The size of the pores formed affects the performance of the membrane in determining the pure water flux value. From Figure 2.4 it can be seen that the membrane with the DMSO solvent has a greater porosity value than the membrane with the NMP solvent. Where as the B2 membrane with 2% silica additive has a porosity value of 16.88%. This can also be seen from the results of SEM photo analysis (Figure 3.1) which shows an increase in the number and size of membrane pores which are larger than other membranes. Having a high porosity value can also increase the permeation flux and this is very beneficial for membrane performance [9].

Membrane Performance

Analysis of Pure Water Flux Test on Membranes

To determine the amount of flux contained in the membrane using a filtration test. This flux test analysis was carried out using pure water. Water will flow through the membrane per unit surface area of the membrane and per unit time with a pressure boost entering the filtration test equipment used to determine the pure water flux. The flux value is measured to determine the capacity of the membrane to pass various amounts of feed [7]. The pure water flux in this type of membrane can be seen in Figure 3.5

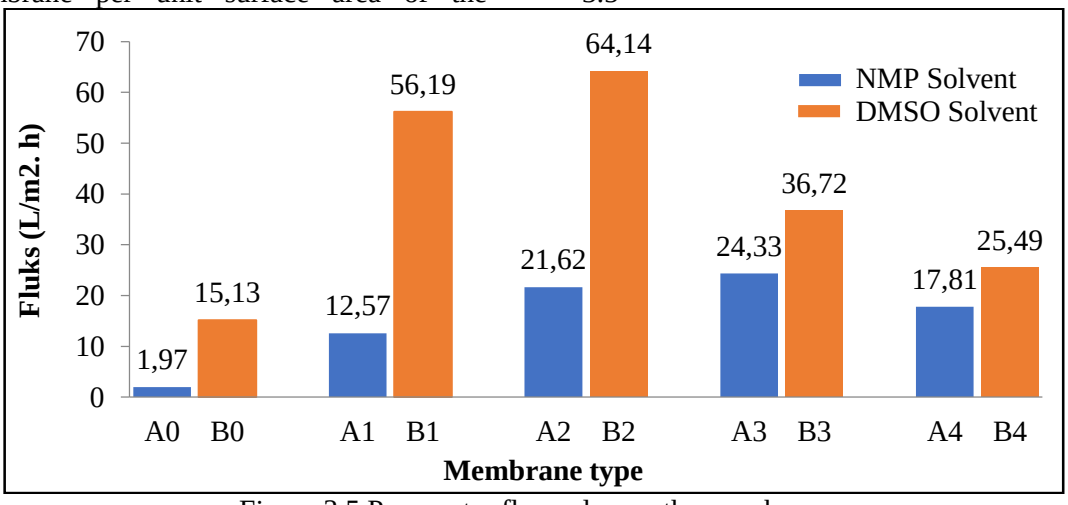


Figure 3.5 Pure water flux value on the membrane

It can be seen that Based on Figure 3.5 shows that the pure water flux value in the membrane modified with the addition of silica additives shows a pure water flux value that is higher than the flux value of the unmodified membrane. This is because the addition of silica additives results in the formation of pores in the cross-sectional membrane, so that the flux through the membrane will be higher. The increased flux value is also caused by the addition of additives that make the membrane surface hydrophilic, allowing water molecules to be more easily absorbed and increasing the amount of water that comes out of the membrane. The pure water flux value is also influenced by membrane porosity. The choice of solvent has an important role in the value of pure water flux and membrane porosity. High membrane porosity produces high pure water flux values. Membrane B2 produces the highest pure water flux value because it has the highest porosity among other membranes [7].

Analysis of the Rejection Capability of the Membrane

Membrane rejection is the ability to retain solutes that cannot pass through the membrane. Determination of the rejection ability is measured using a visible spectrophotometer against a humic acid solution. The rejection ability of humus acid particles on various types of membranes can be seen in Figure 3.6

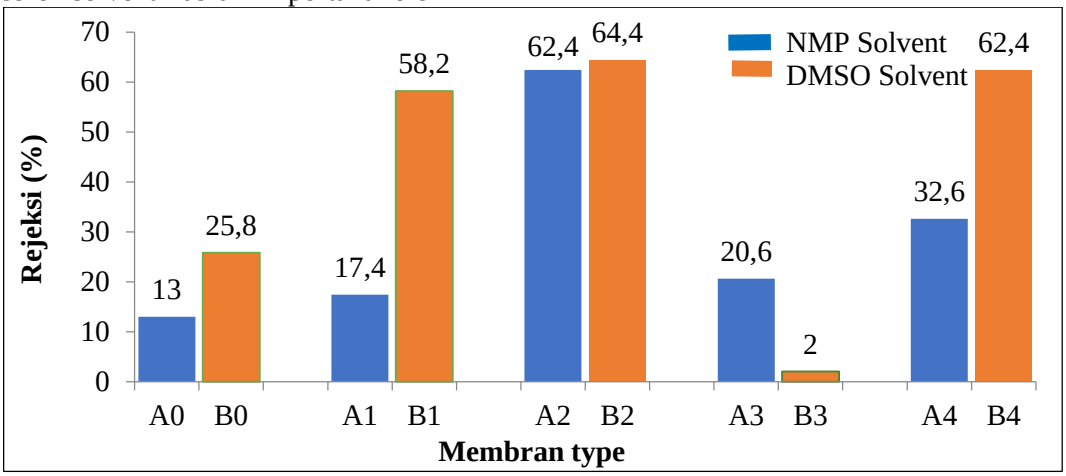


Figure 3.6 Rejection of humic acid solution on the membrane

The B2 membrane has the highest rejection capacity, namely 64.6%, this is because the B2 membrane has larger pores and a thicker dense layer than other membranes. Due to the large amount of humic acid that will be retained on the surface of the membrane and cause the separation process to be better, the permeate that comes out has a lower concentration than the feed when it is entered [10].

Analysis of Fouling Resistance Values on Membranes

The presence of fouling on the membrane can reduce the production rate of the water produced and change the selectivity of the membrane used. Fouling can also damage the membrane because the membrane will need to be washed more often and inhibit other activities on the membrane. Testing the fouling resistance value is useful to see the durability of the membrane in future industrial applications. Membrane flux will generally decrease due to pore blockage by particles passing through the membrane [11].

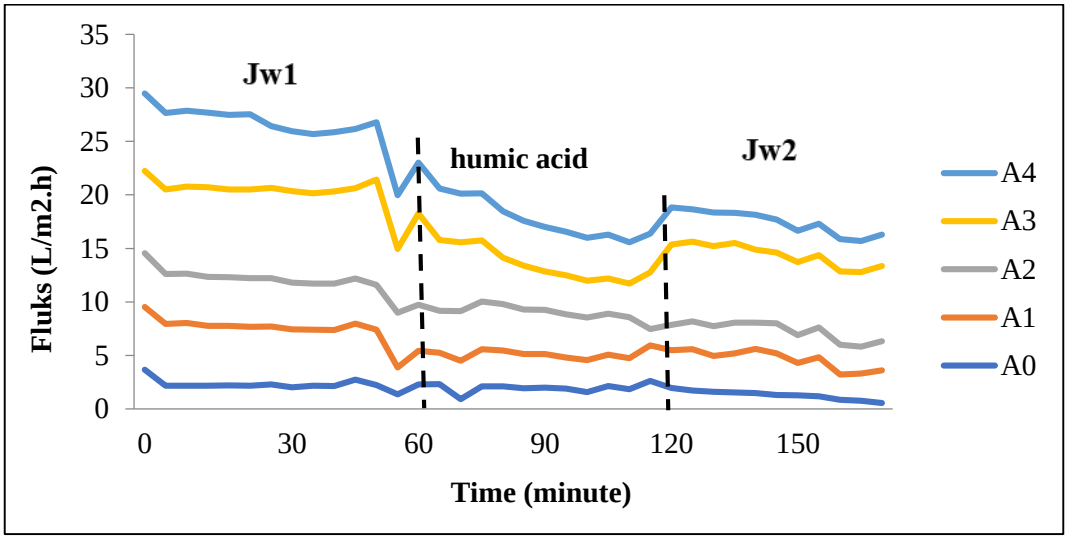


Figure 3.7 Fouling resistance on membranes with NMP solvent

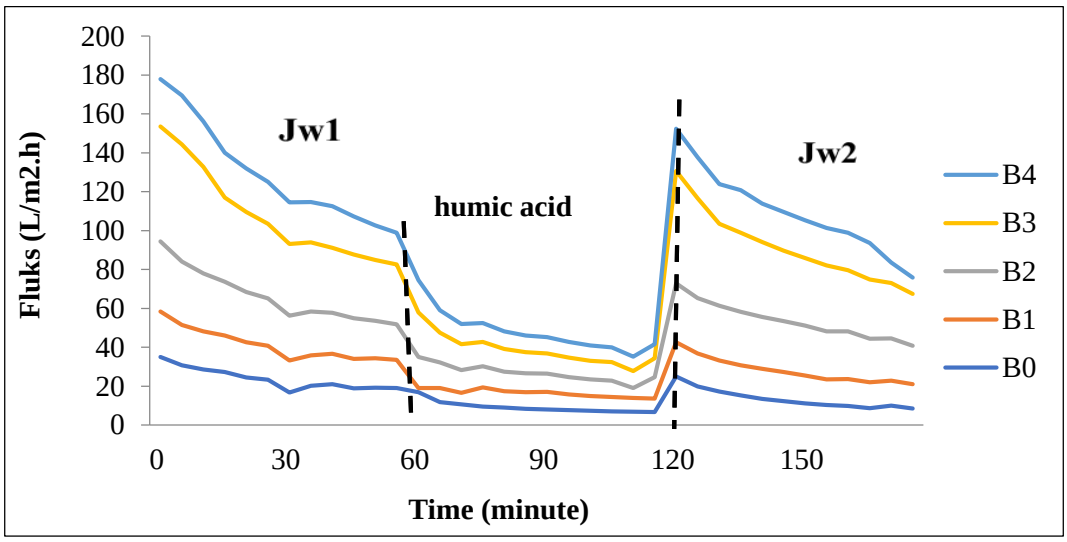


Figure 3.8 Fouling resistance on membranes with DMSO solvent

To see the membrane's resistance to fouling, 3 stages are carried out, in the first stage the membrane is filtered using pure water called (Jw1) for 60 minutes, then passed through a humic acid solution as an artificial solution with a concentration of 50 ppm for 60 minutes, then a backwashing stage is carried out for 10 minutes. then the final stage is passed through pure water called (Jw2) for 60 minutes.

The presence of fouling on the membrane can be observed from the decrease in water flux during the filtration process. Figure 3.7 and Figure 3.8 show the membrane flux performance carried out in a three-step filtration experiment. In the first step, all membranes produce a high flux of pure water (Jw1). In the second step, the flux obtained decreased when pure water was supplied and replaced with a humic acid solution. This decrease was caused by fouling on the membrane (cake formation) due to the accumulation of humic acid particles on the surface, resulting in a decrease in flux in the first minutes of operation. To remove humus acid fouling that has accumulated in the membrane, it is necessary to carry out a backwash process and re-filter the pure water in the membrane. The cleaning effect can be judged from the water flow after backwash (Jw2). The closer the Jw2 flux value is to the Jw1 flux value, the easier the membrane is to clean and the better its antifouling properties. The increase in membrane flux is caused by an increase in the number and size of membrane pores formed due to the addition of additives. Based on the flux test results, the membrane with NMP solvent has the

highest flux value, even after backwashing, the membrane can pass water with a flux value that is close to the pure water flux value [12]. In Figure 3.9, you can see the total fouling value that occurs in each type of membrane.

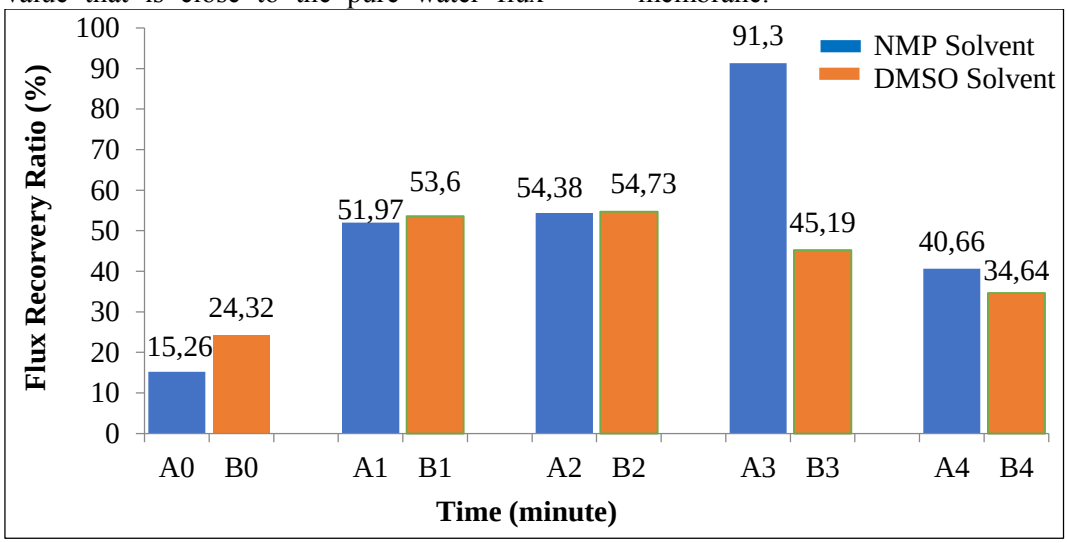


Figure 3.9 Graph of antifouling properties

Based on Figure 3.9, it can be seen that the membrane with the addition of 3% silica additive, namely A3, has a higher flux recovery ratio (FRR) value. This is because the closer the flux value Jw2 is to the flux value at Jw1, the easier it is to clean the membrane, which will have better antifouling properties. Judging from the membrane flux value, the membrane can still be used for the filtration process. This can be from handling the membrane during backwashing which increases the value of the membrane flux after passing the humic acid solution. Even though the water flux did not reach the original level, the flux value remained close to the initial flux value, which shows that the modified membrane has good anti-fouling properties [13].

CONCLUSION

Membranes with DMSO solvent have larger pores compared to membranes with NMP solvent which have fewer pores. The addition of silica additives with DMSO solvent was able to increase the porosity value of the membrane, with the highest porosity value on the membrane, namely B2, at 16.88% and the membrane with the addition of silica additives had the highest pure water flux, namely 64.14 L/m2.h. Membranes with the addition of silica additives have the highest rejection capacity of humic acid solutions with DMSO solvent, namely 64.4%. The addition of silica additives can overcome membrane fouling. Where the best fouling resistance value is found in the A3 membrane with NMP solvent with a flux ratio recovery value of 91.3%.

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