Synthesis of Cellulose Acetate/Polysulfone Hollow Fiber Membranes with Hydrophic Surface Modification for Desalinastion Application

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**Abstract.** Hollow fiber membrane technology with a Direct Contact Membrane Disitilation (DCMD) configuration is a clean water treatment technology that has been widely developed. It is promising with its stable characteristics and produces high permeate flux. Celullose acetate based hollow fiber membranes with polysulfone (PSf) loading have been successfully synthesized using spinning technique. To prepare hydrophobic characteristics, surface modification has been carried out with Low Density Polyethilene (LDPE). Analysis of hydrophobicity properties was measured using water contact angle, while functional groups and morphology were analyzed using FTIR and SEM, respectively. The SEM image show that the membrane morphologhy looks like finger-like structure. The FTIR spectrum shows absorption at 1489 cm-1 and 2851 cm-1 indicating the presence of S=O and C=C, respectively. Hydrophobic properties are shown by a contact angle value 94% at 5% LDPE loading. Performance test show that the CA/PSf membrane with 5% LDPE content has a maximum flux 3.13 kg/m2h and salt rejection of 99.24%. In conclusion, hollow fiber membranes with surface modification using LDPE promise to increase their hydrophobic and performance.

# INTRODUCTION

The global water crisis is worsening due to climate change. In 2016, 930 million people experienced water scarcity, while water consumption increased by an average of only 1% per year over the past 40 years. Water is essential for meeting daily needs such as cooking, washing, and drinking 5 [1]. It is also crucial for the survival of humans, animals, and plants. Additionally, water is highly necessary in the agricultural industry [2]. Indonesia is among the countries with a high risk of water scarcity, with a score of 3.26, ranking 51st on the list of countries with the highest water scarcity [3]. To address the water resource issues and make water suitable for drinking and other clean water needs, desalination is used.

Desalination is the process of removing salts and dissolved minerals from seawater or brackish water to produce fresh water that is suitable for consumption. This process is an important solution to address the scarcity of clean water. This process is considered as one of the most potential alternatives both in terms of durability and technology. The membrane technology that we use is distillation membrane technology. Membrane distillation is a water treatment technology that uses a semipermeable membrane to separate water from other solutes, such as salts and minerals. Membrane distillation involves heating seawater to produce water vapor, which is then condensed back into fresh water after cooling.

Distillation membranes are usually made of polymers such as polyvinylidene fluoride (PVDF), polyethersulfone (PES) or polysulfone (PS). However, this process requires large amounts of energy to heat seawater to boiling, resulting in higher production costs compared to other seawater treatment technologies. Membrane distillation holds promise in seawater desalination as it can produce high-purity freshwater of up to 99.9% without harmful chemicals. The technique relies on the difference in vapor pressure of the compounds in the mixture, where liquids with higher vapor pressure will have lower boiling points. The membrane distillation process applies repeated heating with different pressures at each stage to produce fresh water from seawater [4].

Researchers will use cellulose acetate which has great potential as a membrane material due to its asymmetric structure with a thin active layer. The advantages of cellulose acetate as a membrane material are its ease of production and renewable raw materials [5]. Cellulose is a non-toxic and recyclable polymer widely used in the industry, both in its natural form and chemically modified. Cellulose acetate membranes can operate at pH 2-10 and a maximum temperature of 50°C, are hydrophilic, environmentally friendly, biodegradable, and cheaper than other polymers such as polysulfone [6]. To improve the mechanical properties of the membrane, polysulfone was added which is resistant to high temperatures, various pH, chlorine, and easy to process. Even so, polysulfone is hydrophobic and susceptible to fouling. Therefore, Low Density Polyethylene (LDPE) was added to improve the antifouling ability of the membrane. LDPE has strong, flexible properties and has good durability when applied to chemical solvents. LDPE can be used as a coating material for coating in membrane fabrication. In this study, LDPE compounds are used as additive compounds in the polysulfone (PSf) membrane fabrication process which aims to improve the hydrophobicity of the membrane which will be applied to the water treatment process.

Based on research by Peng Wan et al. (2017), HFM PSf was successfully modified with zwitterionic polymers using ATRP. The membrane modified with Carboxybetaine methacrylate (CBMA) showed the best antifouling properties compared to the charged membrane and pure HFM PSf. However, in this study, we modified the pure HFM PSf by adding LDPE hydrophobic additives to form a coating surface membrane [7]. In research by Retno Ariadi Lusiana, et al (2019) proved that the addition of PEG and the sulfonation process using sulfuric acid to convert polysulfone has improved the physical properties and hydrophilicity of the membrane. The water absorption of the membrane increased by 125-300%. The mechanical strength increased by 2-5 times, and the degree of hydrophilicity increased compared with the pure polysulfone membrane. Therefore, in this study, we will use LDPE as an additive material so that the membrane can be hydrophobic, that is, the membrane does not absorb water [8]. In this study, it is expected that the use of polysulfone material with the addition of cellulose acetate additives and the addition of sulfonate is expected to produce a membrane that is strong, durable and produces high permeate flux. Thus, an alternative membrane will be obtained for application in the desalination process in seawater with good performance.

**MATERIALS AND METHODS**

**Materials**

Cellulose acetate is the main ingredient in the membrane. The molecular weight of Cellulose Acetate (CA, 30.000 g/mol, Chemical Book), Polysulfone were used as additives. The molecular weight of PSf is 35.000 g/mol, Hydrophobic surface-modifying with Low Density Polyethylene. The molecular weight of LDPE is 500.000 g/mol, Toluene (99.8%) were used as solvents for coating agent solution.N-Methyl-2-Pyrroliodine (NMP, 99%, Sigma Aldrich), water, epoxy (resin and hardener), and ethanol (>98.5%, Sigma Aldrich).

**Preparation of Cellulose Acetate/PSf Based Hollow Fiber Membrane**

In this research, the process used is using the Phase Inversion method. The phase inversion technique is a process of controlled change of polymer from liquid phase to solid phase. In this principle, a solution whose initial state is stable then instability occurs in the phase change (demixing) from water to solid. The phase change will begin with a change in one layer of solution into two layers. The advantage of this method is that pore formation can be controlled and can be used in a variety of polymers. Cellulose acetate membrane is made by phase inversion technique, which is a change in the form of polymer from liquid to solid under controlled conditions. The controlled conditions referred to here are the time of evaporation of the solvent when making the membrane [9]. In the phase inversion method with immersion precipitation, namely by printing a polymer solution on a buffer which will then be dipped into a coagulation bath containing non-solvents. Precipitation occurs due to the exchange of solvents with non-solvents [10].

In the next process, namely fabrication using a hollow fiber membrane spinning tool with the main material in the form of cellulose acetate. Currently, membranes using cellulose acetate are experiencing increased development for processing river water, groundwater and also sea water. The advantages possessed by cellulose acetate itself include having polar polymer properties and being able to rejection salt [11].The use of cellulose acetate as a membrane base material has several advantages as well, namely very selective in the adsorption process, soluble in various types of solvents, and also hydrophilic [12]. However, cellulose acetate as the basic material of this membrane has disadvantages, such as a high degree of expansion, sensitivity to temperature changes and also resistance to acids [13]. Therefore, other materials are added in the form of polysulfone (PSf). This is because polysulfone has good mechanical quality and chemical stability, has resistance up to 200 ºC and has relatively large pores so that the water flux is also large. In this study using Direct Contact Membrane Distillation (DCMD) configuration. This is because DCMD is a simple configuration that can produce high flux values and can be used in the desalination process [14].

## TABLE 1. *Variable composition of hollow fiber membrane*

|  |  |  |  |
| --- | --- | --- | --- |
| **Variable** | **Value (wt%)** | | |
| Cellulose Acetate | 15 | 15 | 15 |
| PSf | 5 | 5 | 5 |
| NMP | 80 | 80 | 80 |
| LDPE | 0 | 1 | 3 |

The hollow fiber membrane solution is prepared with a 100% concentration. Cellulose acetate, as the main material, and polysulfone as an additive are dried at 60ºC for 6 hours to remove moisture. N-Methyl-2-Pyrrolidone (NMP) is used as the solvent according to the variables in Table 1. 15% cellulose acetate is stirred with a magnetic stirrer at 380 rpm and 60ºC for 24 hours until homogeneous, then 5% polysulfone is added and stirred for 2 hours until homogeneous. The solution is left at room temperature for 24 hours to eliminate air bubbles. The process continues with the fabrication of hollow fiber membranes using a hollow fiber membrane spinning device according to the operating conditions in Table 2. The formed membranes are cut and soaked in distilled water for 24 hours for phase inversion. In the manufacture of hollow fiber membrane solution adjusted to variables that have been set with a concentration

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| --- | --- | --- |
| TABLE 2. *Hollow fiber membrane spinning operating conditions* | | |
| **Spinning Condition** | **Spesification** | **Unit** |
| Spinneret OD/ID | 0,8/0,4 | mm |
| Dope Solution | CA/PSf/NMP | - |
| Bore Fluid | NMP : Aquades  50 : 50 | - |
| Bore Flow Rate | 0,5 | mL/min |
| Air Gap | 5 | cm |
| Treatment Bath | Water | - |
| Coagulation Bath Temp. | 27 | ºC |
| Drum Speed | 5 | rpm |
| Gear Pump Speed | 5 | rpm |

In this study, the spinning process was carried out with the operating conditions used can be seen in table 1. The spinning condition parameters used are as follows: (1) Out Diameter/in diameter (OD/ID) spinneret is to determine the diameter size of the hollow fiber membrane cavity. The spinneret size that has been determined is 0.8/0.4; (2) Dope solution contained in the manufacture of hollow fiber membranes in the form of cellulose acetate/polysulfone/NMP; (3) The bore fluid used in this study is NMP: distilled water (50: 50 ml). Where, this bore fluid serves to keep the inside of the membrane (lumen) hollow; (4) In this study, researchers used a bore fluid flow rate of 0.5 ml/min; (5) The air gap distance or commonly referred to as the air gap is the distance between the spinneret and the water surface in the coagulation bath. If the air gap distance is greater, the thickness of the membrane will be smaller as a result of the solvent evaporation process and the efficiency will be smaller. The air gap parameter used in this study is 5 cm. The air gap parameter is 5 cm, this is because the physical surface of the membrane formed is smoother than the higher air gap distance.

**Modification of Cellulose Acetate/Polysulfone/LDPE-based Hollow Fiber Membranes**

The membrane modification carried out is the manufacture and addition of a coating that will be applied to the outer surface of the membrane. In the use of the coating there is LDPE as a hydrophobic material and Toluene as a solvent. The coating method used is dip-coating where the hollow fiber membrane is dipped into the coating solution for 30 seconds so that the LDPE will coat the outer surface of the hollow fiber membrane.

**Fourier Transform Infra-Red**

To make sure that the LDPE material was successfully added to the membrane, a Fourier Transform Infra-Red (Thermo Scientific, Nicolet iS10) instrument was used for characterization. The hollow fiber membrane was analyzed in the wavelength range of 500 to 4000 cm-1.

**Scanning Electron Microscope**

The Scanning Electron Microscope (Hitachi, model : TM3000 tabletop microscope) was used to observe membrane morphology: surface and cross-sectional area. For preparing samples for surface and cross-sectional analysis of the membrane, the hollow fiber membrane samples are first immersed in liquid nitrogen for a few seconds until they harden. After immersion, the samples are broken at both ends using tweezers. The resulting sample pieces will be used for SEM cross-sectional examination.

**Water Contact Angle**

The water contact angle is done in a simple way, where the membrane fiber is placed between two holders equipped with clamps to hold the position of the membrane. The droplet method was used to measure the contact angle seen from the fiber horizontal surface. A total 1 μml of water droplet was introduced on the surface of the fiber, and the image profile of the drop was shown by the software.

**Porosity of the Membrane**

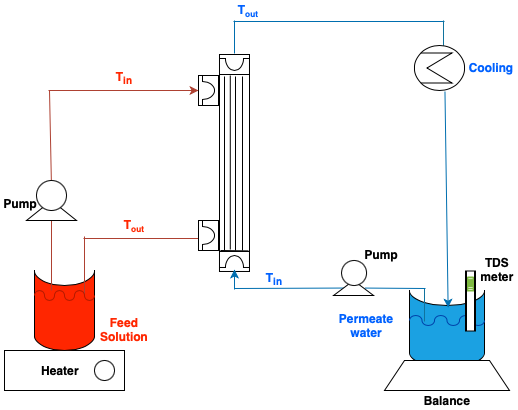
Membrane porosity testing using the gravimetric method. The data that has been obtained is calculated using the following formula was used :

(1)

Where is the weight of the membrane in the wet state (gr), is the weight of the membrane in the dry state (gr), A is the membrane area (m2), is the thickness of the membrane (m), and is the density of water (0.998 gr/cm3).

**Membrane Performance**

The performance of the distillation membrane is evaluated based on permeate flux and salt rejection. Hollow fiber membranes are used in Direct Contact Membrane Distillation (DCMD) for seawater desalination with a 3.5%wt salt solution (NaCl solution), matching seawater concentration [15]. The feed solution is heated to 70ºC, increasing permeate flux due to the large temperature gradient [16]. The distillate flow is maintained at 25ºC with the same flow rate for feed and distillate. Desalination process steps: First, distillate water is passed through the membrane lumen to check for leaks. Next, feed water is flowed for performance testing.



## FIGURE 1. *Direct contact membrane distillation*

The dried membrane is assembled into a shell using tee fittings and reducer fittings, joined with epoxy resin to form a 20 cm long membrane module. Permeability is tested through DCMD with a 3.5%wt salt solution as the feed. The hot feed flows through the fiber shell, while cold water flows through the membrane lumen with the help of 2 peristaltic pumps. Both streams flow co-currently at 0.50 m/s with controlled constant temperatures. The temperatures of the input and output streams are monitored, and the quality of the permeate/distillate is checked using a conductivity monitor.

The permeate flux can be calculated using the equation :

(2)

Where J is the permeate flux (kg/m2h), is the mass of the permeate (Kg), A is the surface area of the hollow fiber membrane (m2) and is the time interval (h).

The membrane performance for the desalination process was also determined by its salt rejection. A conductivity meter was used to monitor the permeate cold water quality. The percentage of rejection was calculated based on the following formula :

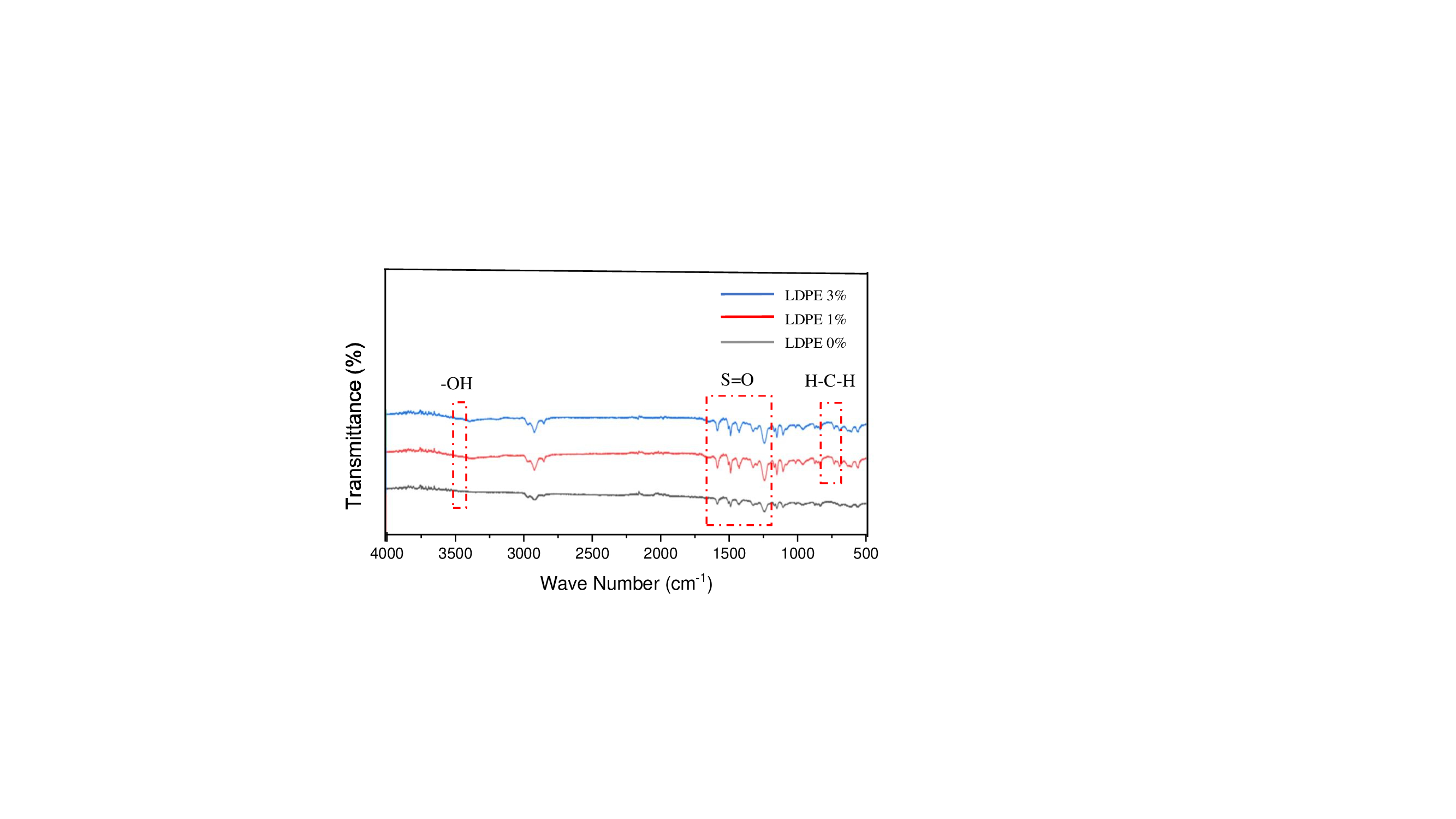
(3)

Where R is salt rejection (%), Cf is salt concentration in feed solution (μS), and Cd is salt consentration in permeate (μS).

**RESULTS AND DISCUSSIONS**

**Fourier Transform Infra-Red**

The structure and functional groups of the membrane can be analyzed using a Fourier Transform Infra-Red (FTIR) instrument. In the analysis with the FTIR instrument, several pieces of hollow fiber membrane strands were placed in the FTIR analysis pellet and then analyzed in the wavelength range of 500-4000 cm-1. This test aims to determine the membrane structure by analyzing the frequency of the FTIR spectra functional groups. The graph below is the result of the functional groups contained in each membrane. The -OH group indicates the presence of cellulose acetate groups which can provide good permeability properties and adequate mechanical strength [17]. The H-C-H group indicates the presence of LDPE groups [18]. The S=O group indicates the presence of polysulfone groups [19].



### **FIGURE 2.** FTIR test results of hollow fiber CA/PSf/LDPE membrane (LDPE: 0%, LDPE: 1%, LDPE: 3%)

**Morphological Structure**

The morphological structure analysis of membrane surface and cross-section was performed by SEM. The membrane has an asymmetric structure that resembles a finger-like structure and there are areas with a sponge structure in the center of the cross section and pores in the outer and inner layers of the membrane. Membrane without 0% LDPE coating (a) has an intact structure and a smooth surface, as well as a regular cross section. The number and size of pores on the surface of the membrane without LDPE coating is relatively few and small compared to the membrane with the addition of LDPE coating. In membranes with coating variations of 1% (b), 3% (c), it can be seen that the membrane structure still looks intact. However, when viewed from the increasing concentration of LDPE, it can be seen that the membrane surface increasingly looks rough and uneven. Hashemi et al. 2019, stated that there is an unbalanced interaction between LDPE and polymers (cellulose acetate and polysulfone) in the membrane mixture, which can cause structural non-uniformity in the membrane [20]. This is also the same with the pores formed in the membrane. The greater the concentration of LDPE, the more and larger the pores formed on the membrane surface. Rahimpour et al. 2012, stated that this is because the addition of LDPE coating with increasing concentration can cause large pores to form due to phase separation between LDPE and other polymers in the membrane mixture [21]. This is also due to the large number of clumps of LDPE found on the membrane surface.

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|  |  |
| (a) | |
|  |  |
| (b) | |
|  |  |
| (c) | |

### **FIGURE 3.** The SEM image for (a) CA/PSf/LDPE 0%, (b) CA/PSf/LDPE 1%, and (c) Ca/PSf/LDPE 3%.

**Water Contact Angle CA/PSf/LDPE**

Contact angle measurement is a common method to identify the hydrophilicity / hydrophobicity properties of a material surface. Figure 3 shows the contact angle result of the fabricated membranes. Water contact angle testing obtained the results of the data obtained. In (a) CA/PSf/LDPE 0% obtained a contact angle of 66º which is hydrophilic which are hydrophilic because the contact angle is <90º. This is because cellulose acetate has a hydroxyl group which is hydrophilic so that it causes the contact angle value to be low [22]. In (b) CA/PSf/LDPE 1% and (c) CA/PSf/LDPE 3% obtained contact angles of 91.9 to 92.1º which are hydrophobic because the contact angle is >90º. This is because with the addition of LDPE coating which is a high hydrophobic polymer with low surface energy so that it can affect the surface roughness of the membrane and cause the hydrophilicity of the membrane to decrease [23]. This is in line with research conducted by Ramli, et. al. 2021, that membrane coating using materials in the form of LDPE can increase the contact angle of 138º - 150º which is hydrophobic because the contact angle is >90º [24]. The increase in the level of hydrophobicity obtained is due to an increase in the precipitation rate of the coating solution used to form the microstructure and nanostructure of LDPE on the membrane surface and can produce a hydrophobic layer.

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| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |

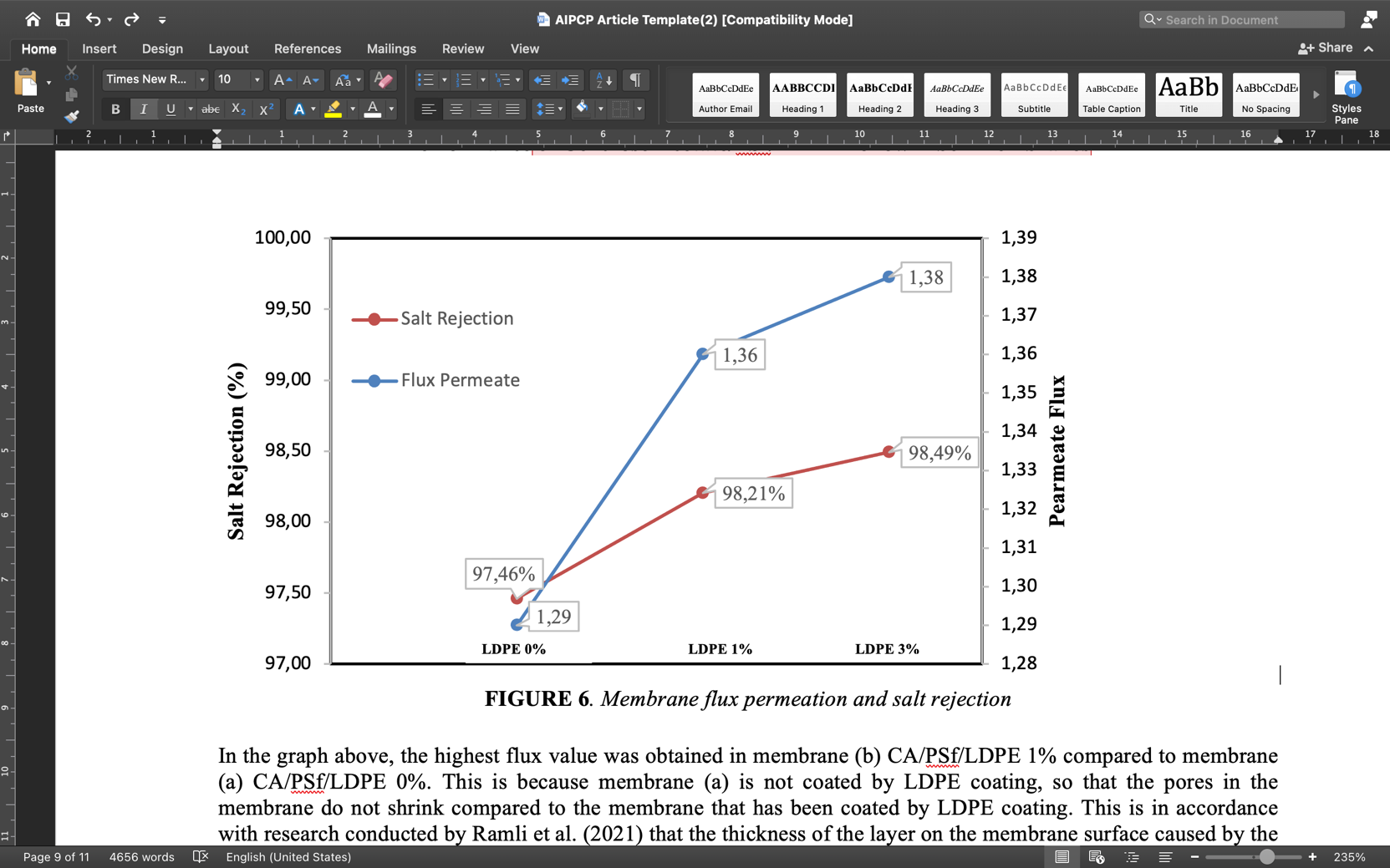
### **FIGURE 4.** Water contact angle measurement result for (a) CA/PSf/LDPE 0%, (b) CA/PSf/LDPE 1%, and (c) Ca/PSf/LDPE 3%.

**Porosity Analysis**

Membrane porosity testing aims to measure the number of pores produced in the membrane structure. Porosity is an important parameter in membrane characterization because it can affect the performance of a membrane. The porosity test results of the CA/PSf/LDPE membrane were obtained. In (a) CA/PSf/LDPE 0% has the highest porosity value which is 74.86% compared to the membrane with the addition of LDPE coating where the increasing concentration of LDPE coating, the decreasing porosity. This is due to the addition of LDPE which can significantly reduce porosity. The addition of LDPE to the membrane will occur LDPE phase separation in the membrane which will experience a decrease or delay which will result in lower porosity [24]. Based on the results of the porosite test, the best membrane to be applied to water desalination is membrane (c) CA/PSf/LDPE 3% with porosity of 67.87%.

### **FIGURE 5**. The porosity graph for (a) CA/PSf/LDPE 0%, (b) CA/PSf/LDPE 1%, and (c) Ca/PSf/LDPE 3%.

**Performance of Cellulose Acetate/PSf/LDPE Hollow Fiber Membranes**

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### **FIGURE 6**. Membrane flux permeation and salt rejection

In the graph above, the highest flux value was obtained in membrane (b) CA/PSf/LDPE 1% compared to membrane (a) CA/PSf/LDPE 0%. This is because membrane (a) is not coated by LDPE coating, so that the pores in the membrane do not shrink compared to the membrane that has been coated by LDPE coating. This is in accordance with research conducted by Ramli et al. (2021) that the thickness of the layer on the membrane surface caused by the level of hydrophobicity of the high concentration of LDPE can be a major contributor in increasing mass transfer resistance. So, the increasing concentration of LDPE will cause an increase in permeate flux in the membrane compared to membranes without coated by LDPE. It was found that the highest salt rejection value produced was in membrane (c) CA/PSf/LDPE 3% around 98.49%. This is because the membrane is well coated by LDPE. This shows that the LDPE hydrophobic layer on the surface membrane only allows the transfer of water vapor through the micro membrane, (Ramli, et.al, 2021) [25]. This is also in line with research conducted by (Ramli et. Al., 2021) by modifying the PVDF membrane with LDPE coating obtained salt rejection results of 99.9%, and permeate of 4.12 L/m2h. Thus, the addition of LDPE as a coating on the membrane surface can increase permeate flux and salt rejection. However, the addition of LDPE concentration needs to be considered, this is because the surface membrane coating does not penetrate into the membrane pores which can cause a reduction in membrane flux, salt rejection and membrane contact angle.

# CONCLUSION

Cellulose acetate and polysulfondebased hollow fiber membrane with N-Methylpyrroliodie solvent with variation by spinning method and addition of coating in the form of LDPE with concentration of 0%, 1%, and 3% using dip-coating method was successfully carried out so that it can be applied for desalination process of seawater processing.Hollow Fiber CA/PSf membrane without coating still has hydrophilic properties, this is indicated by the contact angle of 66ºC. While the membrane with coating variations of 1% and 3% is 91.9ºC - 92.1ºC. Hollow Fiber membrane based on CA/PSf with NMP solvent and LDPE coating addition has finger-like structure. There are functional groups identified in the form of The -OH group indicates the presence of cellulose acetate groups, the H-C-H group indicates the presence of LDPE groups, and The S=O group indicates the presence of polysulfone groups. The modified CA/PSf hollow fiber membranes with LDPE showed a permeate flux of 3.425 kg/m²h and a salt rejection rate of 98.49%.

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