Vol. 1, No. 1, August 2022, pp. 35-40
p-ISSN: 2963-8577
DOI: 10.57102/jescee.v1i1.14

SYNTHESIS AND CHARACTERIZATION OF ANTIBACTERIAL POLYSULFONE MIXED MATRIX MEMBRANE BY ADDITION OF ZnO

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Abstract

Membrane technology is an emerging alternative in water treatment. This study aims to synthesize a filtration membrane made of polysulfone polymer with the addition of ZnO in order to enhanced the membrane antibacterial/antibiofouling property. The membrane was manufactured via Non-Induced Phase Separation (NIPS) phase inversion of the polymer casting solution. The composition of ZnO was varied into 0%, 0.5%, 1%, 2%, and 3%. The results of the membrane synthesis were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), pure water permeability test, and selectivity test with a turbid meter. The hydrophilic properties of the membrane were analysed by measuring the contact angle, and the antibacterial characteristics were analyzed by the disc diffusion test. Analysis by FTIR showed the presence of a sulfone functional group (S=O) derived from polysulfone polymer and a methyl functional group (C-H) derived from PEG. SEM analysis showed that each variation of the polysulfone membrane had an upper surface structure that was close to the honeycomb structure. The pure air permeability test shows that the membrane is porous and able to pass through pure air. Selectivity test with a turbid meter showed that the membrane is selective to the feed stream that passes through it. Analysis of contact angle measurements showed that the polysulfone membrane surface was hydrophilic. Antibacterial activity analysis showed that polysulfone membrane had antibacterial ability with the largest zone of inhibition with a value 1.8 mm n the membrane with the largest concentration of ZnO.

Keywords:

Antibacterial; membrane; phase inversion; polysulfone

Article History:
Received: July 31st, 2022
Revised: August 7th, 2022
Accepted: August 25th, 2022
Published: August 31st, 2022

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1. Introduction

Every year the need for clean water increases in line with the increasing population and industry growth. But in some circumstances, meeting the need for clean water is a problem that cannot be overcome in several parts of Indonesia, especially during the current pandemic. As in Bolangi Hamlet, Timbuseng Village, Pattallassang District, which has problems with the need for clean water every dry season. Residents in these areas still use well water and rainwater that does not meet clean water standards in meeting their daily needs. Residents admitted that it was difficult because clean water assistance only came once a week and not every resident received the clean water assistance.

In its development to meet the need for clean water, further studies on water resources and processing methods are needed as an alternative. Membranes are an alternative technology that can be used to treat various water resources. Membranes are used for the separation of dissolved organic and inorganic substances, suspended solids, microorganisms, and can be applied to desalination, sewage treatment, and gas separation. In the operation of membranes for water treatment processes, membranes generally will experience fouling events.

Fouling is the deposition of particles, macromolecules, salts, colloids, which are retained on the membrane surface or membrane pore walls, which causes a continuous decrease in flux [1].

Fouling can be classified into three types, namely inorganic fouling, organic fouling, and biological fouling. Biological fouling (biofouling) is formed because of the accumulation and growth of biological species in the form of biofilms on the membrane surface which affects membrane permeability which causes a loss of membrane productivity. Microorganisms are the main cause of biofouling [1].

Biofouling on the membrane can interfere with the operation and even damage the membrane, causing a decrease in the performance of the membrane. However, the process of biofouling formation on the membrane surface can be slowed down. The increasing resistance of biofilms to antibacterial compounds encourages the development of new alternatives to remove these biofilms [2]. One alternative antibacterial agent that can be used is ZnO. ZnO compounds show an antibacterial effect on gram-positive and gram-negative bacteria that are resistant to high pressure and temperature [3]. In this study, the synthesis of polysulfone membranes was chosen with the addition of ZnO as an antibacterial agent to be applied in water treatment.

2. Experimental Method

A. Materials

PSF purchased from Solvay Advanced Polymer, N-Methyl-2-pyrrolidone (NMP) obtained from Merck Milipore, and PEG400 obtained from local supplier were used for membrane casting solution preparation. Zinc oxide (ZnO) obtained from Loba Chemie were used as additives. Nutrient Agar and Nutrient Broth was purchased from local supplier.

B. Membrane Fabrication

PSF membranes were synthesized by additive blending methods and casted via phase inversion method. The detailed composition of the membrane solution is summarized in Table 1. Briefly, membrane preparation consists of dissolving PSF and PEG400 in NMP, blending additives in PSF solution, casting the membrane solution, and immersing the cast solution in a coagulation water bath.

Table 1. Casting solutions composition

Variation	Polymer Solution			Nanoparticle
	PSF (gram)	NMP (gram)	PEG (gram)	ZnO (gram)
Control	18	82	10	0
Sample 1	18	82	10	0.5
Sample 2	18	82	10	1
Sample 3	18	82	10	2
Sample 4	18	82	10	3

C. Membrane Characterization

The membrane surface was analysed by scanning electron microscope (SEM, Phenom Pro X). Membrane chemical structures were analyzed by FTIR (Nicolet™ iS50 FTIR Spectrometer with NIR). Pure water permeability and selectivity tested using syringe filter and turbid meter. Water contact angle (WCA) was determined by the sessile drop technique.

D. Antibacterial Activity Studies

Antibacterial tests were carried out on Gram negative bacteria *E. coli*, using Kirby-Bauer disk diffusion method. The bacterial cultures were sub cultured on Nutrient broth medium. The culture was inoculated on Nutrient agar plates. PSF membrane disks were placed aseptically on the Nutrient agar medium which was already swabbed with the test organism. The experiment was carried out for both PSF membranes, with and without ZnO nanoparticles. The plates were incubated at 37 ^{0}C for 48 h to observe the inhibition zone.

3. Results and Discussion

A. Membrane Morphology

The morphological characteristics of the top surface of the polysulfone membrane were analyzed by Scanning Electron Microscope (SEM) using Desktop Phenom ProX. Each image was taken at 200x magnification. This membrane morphological observation was carried out only on the upper surface of the membrane due to limited equipment in observing the cross-sectional surface of the membrane which required liquid nitrogen. In this study the analysis focused on the pores of the membrane surface, not on the effective pores of the membrane itself.

Fig. 1 shows the results of the surface SEM micrographs on the five membrane variations. Based on the micrograph below, each membrane has an expected surface pores with a honeycomb structure [4]. This honeycomb structure is formed due to changes in the diffusion rate of solvent and non-solvent caused by changes in polymer viscosity when ZnO nanoparticles are added [4].

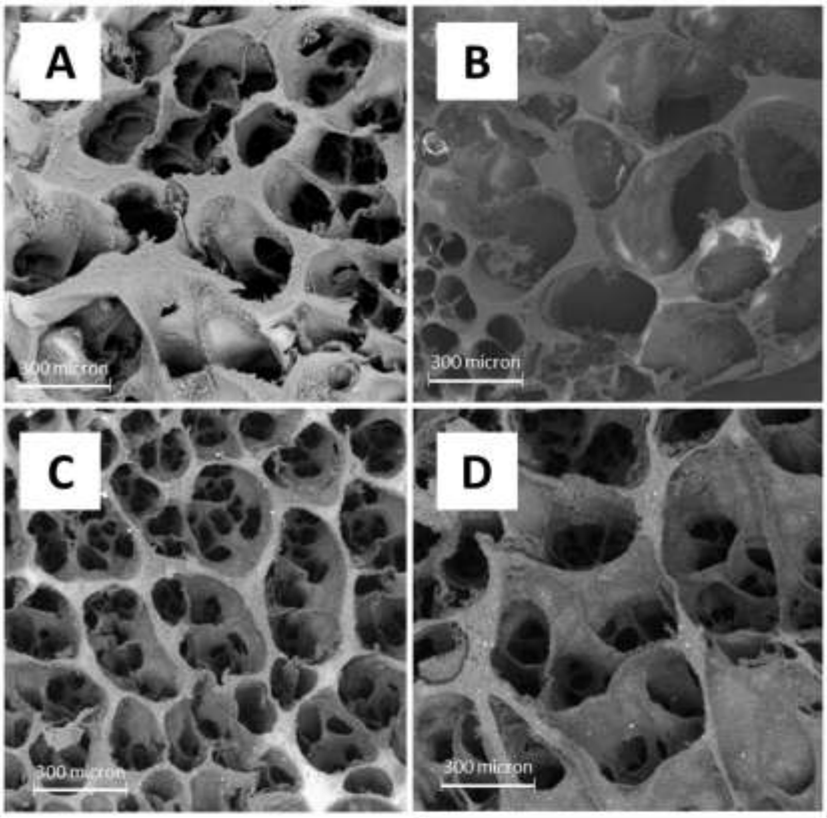

Figure 1. Micrograph of Surface Morphology Polysulfone Membrane
(A: Control, B:Sample 1, C:Sample 2, D:Sample 3)

B. Membrane Chemical Structure

To demonstrate the successful introduction of ZnO, in PSF membrane, all variation membranes were characterized via FTIR analysis (Fig. 2). All membranes showed absorption peaks at around 1,450-1,230 cm^{-1} indicating S=O stretching vibration [4]. The S=O represents the sulfonic groups of PSF. Absorption peaks at around 1,560-1,650 cm^{-1} were found which represent the functional group of C=C of the benzene ring [5]. The stretching vibrations of O-H were represented by the strong, broad band at around 3,650–3,450 cm^{-1}.

Absorption peaks at around 1,200-950 cm-1 were found which represent the functional group of C-O of the ether group [6]. Absorption peaks at around 2,980-2,800 cm^{-1} were found which represent the functional group of C-H represents methyl group of PEG [7]. Thus, the use of zinc oxide in the PSF membrane into the dope formulation does not result in any reaction and new phases or new bonding formation. This was revealed by the FTIR results in this study, which determines that all the PSF bonding patterns in all the PSF and mixed matrix PSF membranes show the existence of the same peaks.

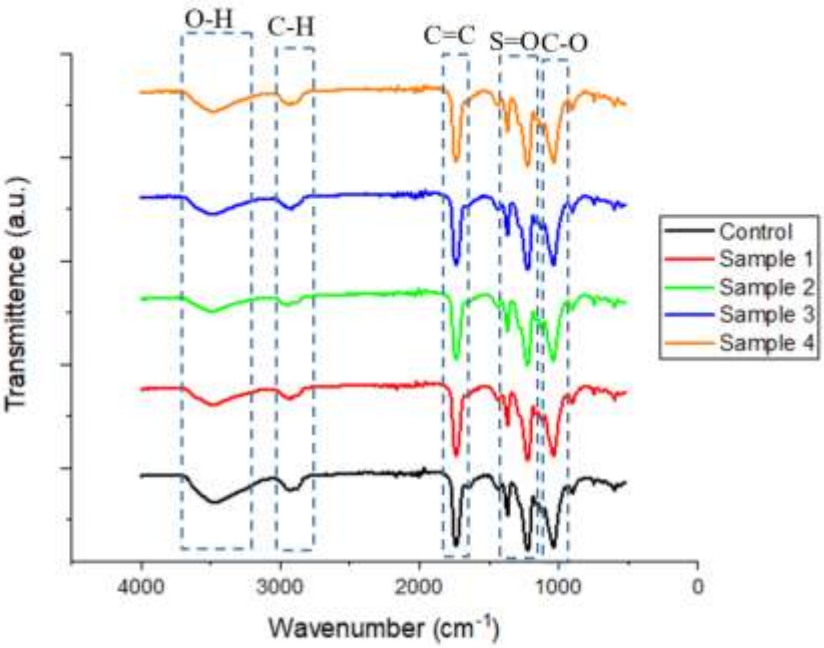

Figure 2. FTIR Spectra of the synthesized polysulfone membrane.

C. Pure Water Permeability & Membrane Selectivity

Pure water permeability tested using syringe filter & syringe filter holder. The result shows all variation of PSF membrane had pore and passed by pure water. Membrane selectivity tested using turbidity meter. The result shows removal percentage value increase as nanoparticle ZnO added as shown in Table 2. The addition of nanoparticle ZnO change surface pore characteristic of the membrane thus poses a different selectivity towards turbidity.

Table 2. Percent removal of suspended solid

Variation	Starch Water
	%Removal
Control	24.71
Sample 1	15.89
Sample 2	27.43
Sample 3	30.23
Sample 4	56.95

D. Membrane Hydrophilicity

Contact angle measurement was carried out to evaluate hydrophilicity of membrane surface. The contact angle values obtained in the measurement of all variations of polysulfone membranes are in the range of less than 90^o which categorized as hydrophilic as shown in Fig. 3. The value of the surface contact angle of the polysulfone membrane decreased with the addition of ZnO nanoparticles, but this decrease was not significant between sample 3 and sample 4. This was due to the formation of ZnO aggregates on the membrane surface which caused pore blocking.

Pore blocking causes the feed stream to pass through the membrane. The decrease in the value of the contact angle of the membrane surface indicates that the level of hydrophilicity of the membrane surface also increases. The level of hydrophilicity of the membrane affects the permeability of the membrane, so that the increasing level of hydrophilicity of the membrane, the more permeable the membrane.

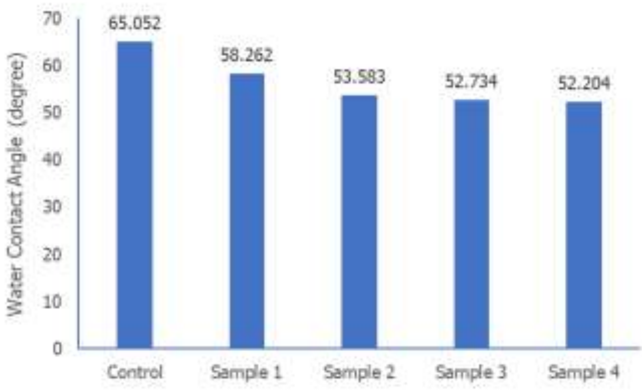

Figure 3. Water Contact Angle of Polysulfone Membrane.

E. Antibacterial Properties

The antibacterial properties of polysulfone membranes were evaluated against E. coli. Here, Kirby Bauer technique was adopted to evaluate the antimicrobial activity. The results are shown in Fig. 4. The pure PSF membrane was used as a control. According to the results obtained, no detectable inhibition Zones were seen for the bare PSF membrane. Conversely, the Zones were observed for ZnO embedded PSF. The diameters of the zone of inhibition around the membranes after one day were measured to be 1 mm, 1.5 mm, 1.7 mm, and 1.8 mm. The inhibition zone formed increases with the increase in the concentration of ZnO nanoparticles. The largest inhibition zone formed was in the sample membrane 4 (addition of 3 grams of ZnO) with a value of 1.8 mm.

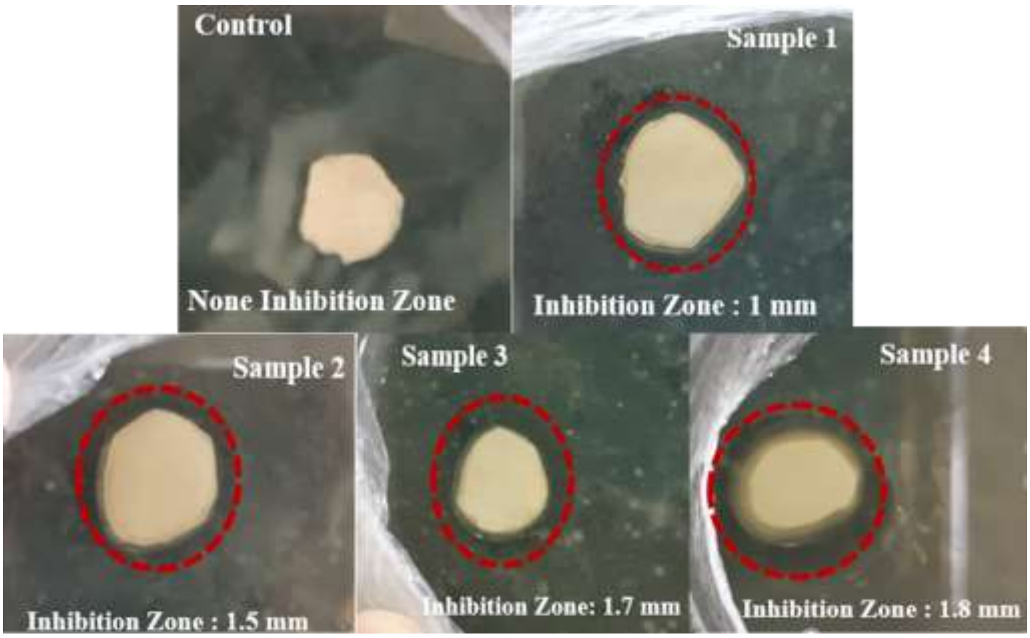

Figure 4. Antibacterial inhibition zone of the synthesized polysulfone membrane

The zone of inhibition was caused by the release of Zn^{2+} ions from ZnO nanoparticles contained in the membrane. The release of Zn^{2+} ions damage the bacterial cell wall and causes protein denaturation. When bound to bacterial cells, Zn^{2+} ions from ZnO nanoparticles damage the bacterial cell membrane and cause leakage in the interior of the cell so that ZnO nanoparticles can enter the cell membrane, disrupting cell metabolism, proteins, and DNA. Then the bacterial cells are damaged, and their development is hampered [8].

4. Conclusions

This research proves that polysulfone mixed-matrix membrane with the addition of ZnO nanoparticles is permeable to pure water and semi-permeable (selective) to turbidity. The addition of ZnO nanoparticles influences the pore characteristics of the membrane surface and affects the level of turbidity selectivity. The addition of ZnO nanoparticles increased the antibacterial activity of the polysulfone membrane which was characterized by the appearance of an inhibition zone. The membrane that produced the best antibacterial activity was sample 4 with an inhibition zone of 1.8 mm against *Escherichia coli* bacteria.

Acknowledgements.

We would like to gratefully acknowledge all staff of the Chemical Engineering Laboratory and Integrated Laboratory of Universitas Pertamina.

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