Enhancement of polyethersulfone (PES) membrane performance by modification with rice husk nanosilica for removal of organic matter in water

S Mulyati¹, M A Armando¹, H Mawardi¹, F A Azmi¹, W P Pratiwi¹, A Fadzlin¹, R Akbar¹, and Syawaliah²

¹Chemical Engineering Department, Syiah Kuala University, Banda Aceh, Indonesia, 23111
²Doctoral School of Engineering Science, Syiah Kuala University, Indonesia

E-mail: sri.mulyati@unsyiah.ac.id

Abstract. This paper reports the effects of rice husk nanosilica addition on the performance of polyethersulfone (PES) membrane. Polyethersulfone membrane (PES) was fabricated by using N-methyl-2-pyrolidone (NMP) as a solvent and rice husk nanosilica as a modifying agent. The influence of the rice husk nanosilica additive on the characteristics and performance of the membrane has been studied. Scanning Electron Microscopy (SEM) analysis confirmed that the manufactured membrane has an asymmetric morphological structure consisting of two layers. The upper part of the membrane is a thin layer, meanwhile in the bottom side is a porous layer. The addition of 5% nanosilica resulted in a PES membrane to have a bigger porous than that of pristine PES. The pure water flux of nanosilica-modified membranes were greater in comparison to the pure water flux of unmodified PES membrane. The performance of all membranes were evaluated on humic acid removal. The highest selectivity was showcased by pure PES membrane. The introduction of rice husk nanosilica additive to the membrane declined the selectivity of the membrane to humic acid in the feed solution. This is caused by the pores enlargement and enhanced hydrophilicity of the membrane after modification with rice husk biosilica.

1. Introduction

Water is a fundamental necessity for human. Clean water is used in daily life for drinking, cooking, washing and so on. Drinking water comes from a variety of sources including common sources (rivers, lakes), wells, or bottled mineral water. Water used as drinking water must meet the quality requirements that have been determined, both physically, chemically and bacteriologically. The consumption of water with poor quality will induce negative impacts on public health. Therefore, the proper treatment is needed in order to produce a pathogen and chemicals free clean water [1]. Some of the most common contaminants existing in raw water are hydrophobic organic matters, for instance humic acid, fulvic acid, and humin [2].

The removal of organic compounds in water can be carried out by various methods, including adsorption [3], electrocoagulation [4], anaerobic granular sludge [5], ozonisation [6], Flotation [7],

³ To whom any correspondence should be addressed.
integrated ion exchange - bioelectrochemistry [8], electrocoagulation and dead end microfiltration hybrid process [9]. In addition to those mentioned techniques, membrane technology can also be used as an alternative. A number of researchers have applied membrane technology to reduce organic compounds in water such as using carbon nanotube composite membrane [10], bioreactor membrane [11], and poliamide nanofiltration membrane [12]. Membrane technology owns several advantages namely simple of use, integratable with other processes, chemical-free, and resistant to a wide range of operation temperature [13]. Polyethersulfone (PES) is one of the most commonly used polymers in the production of ultrafiltration membranes, it is due to the characteristic of PES which can work at high temperatures and have outstanding mechanical resistance [14]. In addition, the selection of PES as a membrane material is also due to its affordable availability, ease of utilization, favorable selectivity, excellent permeability, high mechanical and stability to high temperature [15]. However, this polymer has a weakness because it is hydrophobic. This property causes the membrane performance to decrease due to the occurrence of fouling or concentration polarization on the membrane surface.

To reduce the impact of polymerization and fouling on PES membranes, a number of authors have performed a modification on the membranes for instance by irradiation with gamma rays [16], introducing cobalt into the system to produce a nanocomposite membrane [17], blending with polysulfide-amide (PSA) [18]. All those endeavours were aimed to improve the hydrophilicity nature of PES membrane thus the performance could be enhanced by hindering the fouling or concentration polarization phenomenon. The addition of nanoparticles such as SiO$_2$, Fe$_3$O$_4$, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, and ZnO have a significant influence on the characteristics of the resulted membranes, including the membrane top layer, pore size, thickness, hydrophilicity, and other parameters associated with membrane structures such as porosity and macrovoid [19].

In this study, the modification on the PES membrane was done by adding silica nanofiller from rice husk to improve the performance of the membrane. Besides enhancing the separation performance, the utilization of rice husk as an additive is also a green approach because it encourages the reusability of agricultural waste. To produce the nanosilica, the silica was initially isolated of rice husks then it was added to the membrane casting solution as an additive. PES membrane was fabricated by phase inversion techniques. The variables used in this study were the concentration of rice husk nanosilica additive (0, 3 and 5%). The morphological structure of resulting silica and membranes was analyzed by means of Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) was used to evaluate the functional groups of silica and membranes. The pure water permeation experiments of the fabricated membranes were also carried out. Humic acid was employed as a model compound to study the performance of the membranes in terms of flux and rejection against organic matter in feed water sample.

2. Experimental procedure and methodology

2.1. Preparation and Characterization of Rice Husk Biosilica

The raw rice husk was obtained from rice mills around Banda Aceh city. The bio silica was isolated of rice husk by the extraction technique using KOH as a solvent. The rice husk was dissolved with KOH 37% at temperature of 30°C. To precipitate the bio silica, HCl 37% was then added into the solution. Following that, the formed bio silica was separated from the solution by filtration method and followed by the drying process. The particle size of resulting bio silica was reduced by means of ball mill until the smallest possible size was obtained. Furthermore, the bio silica was characterized by using Scanning Electron Microscopy (SEM). This characterization was conducted to examine the morphological structure of the bio silica. In addition, the evaluation of functional groups present in rice husk bio silica was also carried out by using the Fourier transform infrared spectroscopy (FTIR).

2.2. The fabrication of PES–rice husk biosilica modified membrane

The casting solution was prepared by dissolving PES polymer into the NMP solvent. The solution was stirred until homogeneous. The rice husk nanosilica additive of a certain concentration was added
slowly into the solution until completely dissolved. The solution was then poured on a glass plate and casted by using a casting knife. Subsequently, the casted glass plate was dipped into a bath containing non-solvent (water). At that moment, the phase inversion process began and after a few minutes the membrane was detached from the glass plate. After that, the membrane was washed and stored in distilled water before use.

2.3. Filtration Process

The ultrafiltration experiment was performed using a dead-end module with Trans Membrane Pressure (TMP) as a driving force. The TMP used were 3, 3.5 and 4 bars. A membrane sheet with an area of 1.5 x 10^{-3} m^2 was placed in a membrane module with an active surface layer in the direction of feed inlet. The pure water permeability of the membrane was evaluated. This test was carried out using distillate water as a feed solution. Furthermore, the experiment of organic matter removal process was done by using a solution of humic acid as a model sample. The volume of permeate which passed through the membrane was accommodated, the flux and selectivity to humic acid were afterward calculated. Flux was calculated by using equation (1).

\[ L_p = \frac{J}{\Delta p} \]  \hspace{1cm} (1)

Here, \( L_p \) indicates the permeability coefficient (L/m^2.hour.atm), \( J \) is flux (L/m^2.hour), and \( \Delta p \) is pressure (atm).

Selectivity test of the membrane was conducted by using humic acid (HA) solution with concentration of 10 mg/L. The ability of membrane to reject the macromolecules in the feed solution can be calculated by equation (2).

\[ R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \]  \hspace{1cm} (2)

Where \( R \) is coefficient of rejection (%), \( C_p \) is humic acid concentration in permeate, and \( C_f \) is the concentration of humic acid in the feed solution.

3. Results and Discussion

3.1. Characterization of Rice Husk Nano Silica

The morphological and FTIR analysis results of nano silica can be seen in Figures 1 and 2. From the results of SEM analysis it appears that the obtained bio silica from rice husk has a size in the nanometer range (10^{-9}). The silica has a non uniform shape of surface, some of the parts are agglomerated but the nanometer particle size is seen dominating.

From the FTIR analysis it can be observed that the 1099 cm^{-1}, 950 cm^{-1}, and 468 cm^{-1} represent the functional group of siloxane (Si-O-Si) [20] Whereas OH group is typified at a wave number of 3305 cm^{-1} [21].

3.2. Morphology of the Membrane

The surface and cross-sectional morphology of pure and silica-modified PES membranes are presented in Figure 3 and 4. As seen from Figure 3, it is evidencing that there is the appearance of nanosilica deposition on the surface of the silica-modified PES membrane. The result of cross-sectional analysis in Figure 4 shows that the membrane prepared by phase inversion technique has an asymmetric structure, consisting of two layers. The top layer consists of a dense layer and the bottom layer is a porous layer. The diffusion of non-solvent into the membrane (the demixing process) causes the membrane to have a macrovoidal structure. From the figure it is confirmed that all the resulting membranes have a finger-like structure on the sublayer and different macrovoidal forms. The changed in membrane structure may be caused by the addition of the nanofiller, which may have an impact on the growth or suppression of macrovoid [19]. The addition of additive to the membrane has an effect
on the pore size on the bottom layer. The increase in additive concentration results in the enlargement of membrane pore size.

![Figure 1. Morphology of Silica From Rice Husk](image1)

![Figure 2. Spectra FTIR of Biosilica Rice Husk](image2)

![Figure 3. SEM images of the outer surface of PES membrane with and without additive of biosilica](image3)
3.3. Pure Water Permeation (PWP).
Permeability is the ability of the membrane in letting a particular substance to pass through. Pure water permeability is one of the most important characteristics for membranes when applied to the industry. Membrane permeability is determined by measuring pure water flux. Pure water flux reflects pore size, pore size distribution and membrane morphology [22]. The relationship between pure water flux and Trans Membrane Pressure (TMP) is shown in Figure 5.

The filtration experiment in this research was conducted based on pressure-driven, therefore the increase of pressure (TMP) causes the pure water flux passing through the membrane to be larger for all membranes. From the Figure 5, it is clearly seen that the pure water flux is influenced by the addition of rice husk nano silica additive into the membrane casting solution. The pure water flux obtained from experiment using original PES was 35.5 L/m².hour, 0 L/m².hour for PES + 3% additive and 124 L/m².hour for PES + 5% additive. Pure water flux improved with increasing concentration of additives added to the casting solution. The presence of the additive causes the membrane pore size to become larger hence permeate can pass through the membrane more easily.
3.4. Membrane Performances

The removal rate (rejection or selectivity), and permeation are important parameters in determining membrane performance. In this study, water feed containing humic acid with a concentration of 10 ppm was passed through the membrane with a TMP of 3 bar. Flux and rejection of pure PES, PES + 3% additives and 5% additives are shown in Fig. 6. The resulting fluxes show that the addition of the nano silica additive into the membrane affected the permeation rate. The membranes which modified with nanosilica from rice husk showed an enhanced flux in comparison to that of without modification. The addition of 5% rice husk silica has successfully double-augmented the flux of the PES membrane. This is due to pore size enlargement and improved hydrophilicity of the membrane after the silica addition. The percentage of rejection in the experiment is in contrast to the resulting flux. The addition of the additive decreases the selectivity or rejection of the membrane to the humic acid in the sample solution. However, the addition of 3% nanosilica resulted in a rejection which comparable to that of pure PES membrane. The resulting rejection for pure PES membrane, PES + 3% additive and PES + 5% additive were 75.19, 74.39 and 62.25 % respectively.

![Figure 6. Filtration Performance for PES membranes with and without additive. Left: Humic acid flux. Right: Humic acid rejection.](image)

4. Conclusion

PES membrane has been prepared by phase inversion technique and the effect of addition of biosilica from rice husk as additive on membrane characteristics and performance has been studied. SEM analysis showed enlargement of macrovoid size on the silica-modified membranes which leads to increasing of pure water permeation. Filtration performance on humic acid enhanced in terms of flux, meanwhile the solute rejection declined with increasing concentration of biosilica.

References

[1] Bergamasco R, Konradt-Moraes L C, Vieira M F, Fagundes-Klen M R, Vieira A M S 2011 Chem. Eng. J. 166 483-489
[2] Matilainen A, Vepsäläinen M, Sillanpää M 2010 Adv. Colloid Interfac. 159 189-197
[3] Bhatnagar A, Sillanpää M 2017 Chemosphere 166 497-510
[4] Hakizimana J N, Gourich B, Vial Ch, Drogui P, Oumani A, Naja J, Hilali L 2016 Desalination 393 90-101
[5] Tomar S, Gupta SM, Mishra BK 2015 Bioresource Technol. 197 171-177
[6] Cai M, Lin Yp Chemosphere 2016 151 332-338
[7] Xu Zl, Alsalhy Q F 2004 J. Membrane Sci. 233 101-111
[8] Lim Sj, Kim Th 2015 Bioresource Technol. 189 107-112
[9] Ben-Sasson M, Zidon Y, Calvo R, Adin A, 2013 Chem. Eng. J. 232 338-345
[10] Lee J, YeY, Ward A J, Zhou C, Chen V, Minett A I, Lee S, Liu Z, Chae Sr, Shi J 2016 Sep.
Purif. Technol. **163** 109-119

[11] Zhuang H, Hong, X, Han, H, Shan S 2016 Bioresource Technol. **221** 262-269

[12] Zhao Y, Li N, Xia S 2016 Compos Sci. Technol. **132** 84-92

[13] Mulder M 1996 *Basic Principles of Membrane Technology* ISBN: 978-0-7923-4248-9 (Print)
    978-94-009-1766-8 (Online)

[14] Sun W, Chen Cx, Li Jd, Lin, Yz 2009 Chinese J. Polym. Sci. **27** 165-172

[15] Arthanareeswaran G, Starov, Victor M 2011 Desalination **267** 57-63

[16] Zhang X, Niu L, Li F, Yu S, Zhao X, Hu H 2016 Radiat Phys Chem **127** 127-132

[17] Gzara L, Ahmad R Z, Khan S B, Alamry K A, Albeirutty M H, El-Shahawi M S, Rashid M I, Figoli A, Drioli E, Asiri A M -2016 J Taiwan Inst Chem E **65** 405419

[18] Jalali A, Shockravi A, Vatanpour V, Hajibeygi M 2016 Micropor. Mesopor. Mat. 228 1-13

[19] Lin, J., Ye W, Zhong K, Shen J, Jullok N, Sotto A, Van der Bruggen B 2016 Chem Eng Process **107** 194-205

[20] Amutha K., Sivakumar G.2013 Spectrochim Acta A **112**: 219-222

[21] Yusmaniar S B 2007 Jurnal Sains Meteri Indonesia, Edisi Khusus 115-117

[22] Tao M-m, Liu F, Xue, L-x 2013 Ultrason. Sonochem. **20** 232-238