The Effects of Magnesium Hydroxide (Mg(OH)₂) on the Characteristics and Performance of Polyethersulfone Membranes (PES) for Water Treatment

U Fathanah¹,², I Machdar³, M. Riza¹*, N Arahman¹, M R Lubis¹, F Nurfajrina¹, A Yolanda¹, M Y Wahab¹
¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
² Doctoral Program School of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
* E-mail: medyan_riza@unsyiah.ac.id

Abstract. Surface water is commonly used as a source of clean water, but increasingly, surface water is contaminated with various foulants. Humic acids (HAs) are a natural organic matter predominant in ground and surface waters. HAs can reduce the quality of water. This study aims to investigate the results adding magnesium hydroxide, or Mg(OH)₂, to modify polyethersulfone (PES) membranes by determining the characteristics and performance of the membranes. The mixed-matrix membranes were prepared using PES and various amounts of modified Mg(OH)₂ (0%, 1%, and 1.5% wt) as nanoparticle additives. A scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and water contact-angle analysis were used to characterize the membranes, followed by a membrane performance test (flux, permeability, and selectivity of the membrane) using a dead end ultrafiltration module.

It can be concluded that Mg(OH)₂ can improve the hydrophilicity of PES membrane with decreasing the water contact angle from 84.2° (pure PES membrane) to 68° (modified membrane), where ultrafiltration membranes with the highest permeability coefficient are obtained at 1.5% wt of Mg(OH)₂ with a value of 41.94 L/m².h.bar and a rejection percentage of 67.72%.

1. Introduction
The usage of surface water as a source of clean water is increasing however most of a majority of surface water has been contaminated with soluble foulants such as wastewater. It is necessary to remove major organic contaminants in surface water such as humic acids [1]. Humic acids containing carboxyl and phenolic hydroxyl, which can cause the water to become darker, hampering the availability of light in the water [2]. Humic acids are also a substrate in microorganism growth and so make the water more polluted [3].

Membrane technology can be used as a water management alternative in developing countries like Indonesia. There are many advantages of using membrane technology, such as high water quality, consistent water quality, and lower chemical usage [4]. Using membrane technology also allows for selective separation and aseptic operations without generating any byproducts [5].

The membrane used in this study is a polymer membrane of polyethersulfone. A phase inversion technique is used in the preparation process based on the principle of membrane-solution dope phase-change from liquid to solid. PES is a polymer used in membrane manufacturing, known for its...
chemical stability, chemical resistance, and good mechanical properties. However, PES polymer is hydrophobic, so the membrane flux will tend to decline during the operation due to the occurrence of fouling on the membrane[6]. Fouulant build-up on the membrane surface can cause the pore blockage of the membrane, thereby reducing the filtration performance. Fouulant can be either organic depositions (e.g., macromolecules or biological substances), precipitated inorganic depositions (e.g., metal hydroxide or calcium salt), or particulates. Fouulant accumulates on the surface of the membrane, resulting in reduced effectiveness and membrane flux [7].

To improve the membrane performance, the modification is necessary, for instance by adding additive material to the dope during fabrication of the PES membrane. Previous studies have investigated the development of polymer membranes by modifying PES with tetronic 1307 [8], using PES with chitosan to remove nitrate in the water [9], and adding graphene oxide/chitosan to the PES for processing chromium and improving the membrane’s antifouling properties [10].

This study will discuss the modification of PES membranes by adding an inorganic compound, magnesium hydroxide or $\text{Mg(OH)}_2$, to improve the membranes’ performance. $\text{Mg(OH)}_2$ is added as an agent to increase the hydrophilic nature of the polymer PES. Hydrophilic $\text{Mg(OH)}_2$ is used as an inorganic filler to prepare PES/$\text{Mg(OH)}_2$ membranes using a phase inversion method to prevent a decrease in the flux caused by membrane fouling [11].

$\text{Mg(OH)}_2$ is one of the inorganic compounds that have hydrophilic OH groups, making it attractive as an additive in the membrane [12]. In this study, $\text{Mg(OH)}_2$ is added to the PES membrane to improve the membrane’s hydrophilicity for water treatment processes. The effects of adding $\text{Mg(OH)}_2$ will be investigated by examining the characteristics and performance of the resulting membrane.

2. Materials and Methods

2.1 Materials, Some of the chemicals used to manufacture the polymer membrane are polyethersulfone (PES, Ultrason E6020 BASF), N-methyl-2-pyrrolidone (NMP) solvent from Merck, and additive $\text{Mg(OH)}_2$ purchased from Xinglu Chemical Co. Other materials used are deionized water as a non-solvent, a sample of humic-acid solution to test the membrane’s rejection ability, and a set of dead-end filtration equipment.

2.2 Membrane Preparation, All of the membranes were prepared by a phase-inversion method. A dope solution was prepared by dissolving the PES in the NMP solvent with a concentration of 18% wt for all types of membranes. For membrane modification, $\text{Mg(OH)}_2$ was added at 1% and 1.5% wt (see Table 1). The dope solution was sonicated for 30 minutes to prevent the agglomeration of the $\text{Mg(OH)}_2$ and to ensure extraction for air bubbles. The homogeneous PES solution was placed onto a glass plate in a casting machine to produce a wet membrane with a thickness of 250 $\mu$m. This membrane was immersed in a coagulant bath, where the polymer precipitated and the flat membrane formed. The composition of the membrane dope solution with $\text{Mg(OH)}_2$ is presented in Table 1.

| No. | PES (%) | $\text{Mg(OH)}_2$ (%) | NMP (%) | Membrane Name |
|-----|---------|-----------------------|---------|---------------|
| 1   | 18      | 0                     | 82      | A-0           |
| 2   | 18      | 1                     | 81      | A-1           |
| 3   | 18      | 1.5                   | 80.5    | A-2           |

2.3 Membrane Characterizations, Membrane characterization was done by observing its morphology (membrane cross-section) using SEM and the chemical composition of the membrane surface using FTIR equipment, and measuring the hydrophilicity of the membrane using water contact angle analysis (water contact angle meter, Drop Master 300, Kyowa Interface Science Co., Japan.)
2.4 Membrane Performance (Pure Water Permeation and membrane rejection coefficient). The membrane performance in terms of pure water permeability and humic acid selectivity was assessed using a filtration test with the dead-end module. Experiments were carried out using membrane pressure 1; 1.5; 2 and 2.5 bar as the driving force. The membrane was first compacted for 30 minutes to minimize compaction effects. After the flux reached a steady state, the flux was calculated with the following equation [13]:

\[ J = \frac{1}{A} \frac{dV}{dt} \]  

(1)

Where \( J \) is pure water flux (L/m²·h); \( dV \) is permeate volume (L); \( dt \) is the time (hours), and \( A \) is the membrane area (m²). While the equation used to calculate the membrane permeability coefficient \( (L_p) \) [13] is:

\[ L_p = \frac{1}{\Delta p} \]  

(2)

Wherein, \( J \) is pure water flux (L/m²·h); \( \Delta p \) is trans membrane pressure (bar)

Rejection coefficient (R) is the concentration fraction of dissolved substances that cannot pass through the membrane. The equation of rejection coefficient (R) [13] is:

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

(3)

Where,

\( R \) = coefficient of rejection (%)

\( C_p \) = concentration of solute in the permeate (mg/L)

\( C_f \) = concentration of solute in the feed (mg/L)

The relative selectivity of membranes was determined with a humic acid solution containing 50 mg/L humic acid. The filtration condition was exactly the same as that of the permeability test. The concentration of humic acid in the permeate was measured with UV-Vis spectroscopy at a wavelength of 254 nm.

3. Result and discussion

3.1 FTIR analysis

Analysis to determine the difference in the chemical composition of the modified membrane was performed using a Fourier Transform Infra-Red (FTIR) Spectroscopy. FTIR spectroscopy is an instrument that is used to determine the surface functional groups contained in a sample based on molecular interactions in the form of absorbance or transmittance from infra-red rays given to the sample.

The FTIR spectra of PES/Mg(OH)₂ 1% w/w membrane, PES/Mg(OH)₂ 1.5% membrane, and the pure PES membrane are presented in Fig.1. It can be seen that all peak positions of the spectra are precisely the same, including the 1100 cm⁻¹ for sulfone (SO₂) bending vibration, 1230 cm⁻¹ for ether the aromatic (C-O-C), 1465 cm⁻¹ for C-H, and the 1510 cm⁻¹ for aromatic ring [14]. Figure 1 also shows a peak at a wavenumber of 3697 cm⁻¹ on the membrane (A-1) to membrane (A-2), wherein the peak indicates O-H bonds of the Mg(OH)₂ stretching vibration. This peak does not appear on A-0 membrane (pure PES membrane). The O-H group indicates that the Mg(OH)₂ compound added interacts with the PES membrane. O-H can make PES membrane more hydrophilic [15].
3.2 Membrane Morphology

Membrane performance is not only influenced by the pore size but also the number of pores on the surface [16] as seen in the structure of the membrane morphology. The cross-sectional morphology was characterized by SEM, as shown in Figures 2.

![Figure 2](image)

**Figure 2.** The cross-section morphologies of (a) PES and (b) 1.5% w/w Mg(OH)$_2$/PES membranes

As shown in Figure 2, the PES membranes possess an asymmetric structure and a micro-porous finger-like sub-layer. The membrane samples are distinguished by the various amounts of Mg(OH)$_2$ dispersed in the PES solution. In Fig.2 (a) there is no additive. In Figure 2 (b) a membrane with additives added, it can be seen that the macrovoid size of this membrane is greater than that of the pure PES membrane.

Based on the images, it can be concluded that the Mg(OH)$_2$ addition changed the morphology of the membranes by increasing the sizes of the pores. The changes in the pore structure of the membrane are related to the phase inversion process between polymer matrix, solvent, and non-solvent during membrane fabrication [17]. Previous researcher [18] states that the formation of Mg(OH)$_2$ produces macro pores and more pores than PES membrane because Mg(OH)$_2$ is hydrophilic, provides more space for water penetration and further accelerates the rate of water penetration.

3.3 Water Contact Angle

Hydrophilic property of the membranes is an important characteristic that greatly affects the permeability and other membrane performances. It can be investigated by measuring the water contact angle.
contact angle (WCA). A higher WCA indicates that the membrane is more hydrophobic, while lower values can be an indication of more hydrophilic membranes.

![Figure 3. Water contact angle on various types of membrane](image)

As shown in Figure 3, the pure PES membrane has the highest contact angle, 84.2° indicating the most hydrophobic membranes of all evaluated. As the Mg(OH)₂ content increases, the contact angle on membrane surface increases, when the Mg(OH)₂ concentration increases 1% and 1.5% w/w, the contact angle on the membranes surface becomes 69° and 68°, respectively. The decrease of water contact angle indicated the increasing of hydrophilic property of the membrane [19]. Peningkatan sifat hidrofilisitas ini disebabkan oleh kehadiran gugus hidroksil –OH dari aditif MgOH pada matrix membran. Hal ini dapat dikonfirmasi melalui analisa FTIR (Gambar 1).

3.4. Pure Water Flux and Permeability Analysis
The pure water flux (PWF) of the fabricated bare and blended PES membranes is shown in Fig.4. Filtration test equipment used is called a membrane module. The membrane module used is the dead-end ultrafiltration module. Meanwhile, the distilled water is used as the feed in the flux performance test.

![Figure 4. The pure water flux (J) on various types of PES membrane](image)

The pure water flux properties of the prepared membranes were studied by collecting the pure water through a certain time at various pressures in the range of 1 to 2.5 bar. In Fig. 5 it can be seen that the magnitude of the pressure is proportional to the flux generated in the same type of membrane. In A-0 membrane, the flux value is at the operating pressure 1; 1.5; 2 and 2.5 bar by 5.88; 7.59; 8.29 and 10.27 L/m²·h, respectively. Increasing the flux value increases the pressure exerted, because of the formation of the membrane deformation as a result of the high pressure on the feed stream and make the membrane pores become wider [20].
In addition, in Fig. 4 also shows the effect of Mg(OH)$_2$ in various concentrations to the flux value produced. The higher concentration of Mg(OH)$_2$ is added, the higher the value of the flux. The flux of membrane A-1 and A-2 at a pressure of 1 bar respectively 40.01 and 52.89 L/m$^2$·h. Increasing the flux value because of the addition of Mg(OH)$_2$ made a hydrophilic membrane surface easier to absorb water molecules, and increase in the amount of permeate [21].

The relationship between permeability and selectivity is a well-known trade-off in membranes. The coefficient of permeability (Lp) declares the membrane’s ability to pass the pure water at the membrane operating pressure [22]. Fig.5 compares membrane permeability between pure PES, PES/1wt% Mg(OH)$_2$, and PES/ 1.5% Mg(OH)$_2$ membranes. The addition of Mg(OH)$_2$ particles increased the pure water permeability of the PES/Mg(OH)$_2$ membranes. As a control, the pure PES membrane permeability was only 4.12 L/m$^2$·h·bar. However, this value increased to 30.62 and 41.94 L/m$^2$·h·bar for A-1 and A-2, respectively. Based on the overall pure water permeability obtained, the A-1 and A-2 membranes are included in the category of ultrafiltration membranes with permeability coefficient in the range of 10–50 L / m$^2$·h·bar [13].

**Figure 5.** The water permeability coefficient (Lp) of pure water on various types of membranes

Water permeability of the membrane is influenced by the value of water contact angle. The increase in water permeability of the membrane A-1 and A-2 could be explained by the results of water contact angle measurement in Fig.3. There is a tendency for a decrease in the value of water contact angle on the modified membrane with the addition of Mg(OH)$_2$ additive shown in the Figure 3. This shows that the membrane modification with Mg(OH)$_2$ can improve the hydrophilic properties of PES membranes. It affects on the value of the resulted membrane permeability and is a reason for the increase of the membrane permeability.

3.5 Humic Acid Rejection

Membrane selectivity performance is tested through membrane filtration with a humic acid solution. Humic acid is one of the natural organic matters containing water. Filtration membranes with good performance are a membrane with a high water permeability and high solute rejection [17]. The results of flux measurements and rejection analysis of humic acid can be seen in Figure 6.

Based on Figure 6 it can be seen that the highest percentage of humic acid separation with PES membrane is on the membrane A-0 with a value of humic acid rejection of 77.6%. The presence of membrane modification with the addition of Mg(OH)$_2$ additive makes the rejection coefficients decreased in A-1 and A-2 membrane as 68.63% and 67.72%, respectively.

Figure 6 also shows that the flux value of humic acid feed solution increased as the increase of Mg(OH)$_2$. The highest flux of humic acid solution is on the A-2, namely 36.23 L/m$^2$·h. This is influenced by the Mg(OH)$_2$ addition, thus increasing membrane pore make more humic acid passes through the membrane pores. In general, there is a reverse comparison between selectivity and flux membranes. The increase of the membrane pore size would lead to a decline in the selectivity and an
improvement in flux [16]. It can be seen in studies conducted, wherein the A-1 and A-2 produce the rejection value declining at each additive addition. The increase of the additive causes an increase in the hydrophilic property of the polymer membrane and allows the high swelling on the polymer chain to withhold part of the small pores in the membrane (when the large pores keep functioned). In summary, these results show that the higher the value of flux, the lower the selectivity is produced. It results in the lower amount of water to permeate and ultimately the far water flux [16].

Figure 6. Flux and rejection coefficient of humic acid solution on various types of membranes

4. Conclusion
Modifying the PES membrane with additives Mg(OH)₂ has been carried out. The results showed that the presence of hydroxyl group (OH) of Mg(OH)₂ which can be seen from the results of the FTIR analysis. Increased hydrophilic properties can be confirmed with a reduction in the water contact angle of the membrane modified with Mg(OH)₂. Characterization with SEM showed that the membrane is modified with a Mg(OH)₂ solution, asymmetric shape, with the top has a thinner dense layer, while the bottom (support) in the form of finger-like macrovoid. It has more pores and larger size than the original PES membrane without modification. The modified membrane performance gives a permeability coefficient of 41.94 L/m²·h·bar and a rejection coefficient of 67.72%.

References
[1] Guo J, Khan S, Cho S H and Kim J 2019 J. Ind. Eng. Chem. 4555 1
[2] Son M, Kim H, Jung J, Jo S and Choi H 2017 Chemosphere. 179 194
[3] Li Y, Qu G, Zhang L, Wang T, Sun Q, Liang D and Hu S 2017 Sep. Purif. Technol. 180 36
[4] Mirwan A, Indriyani V and Novianty Y 2017 Konversi. 6 11
[5] Taleghani H G, Ghoreyshi A A and Najafpour G D 2018 Biochem. Eng. J. 132 52
[6] Arahman N 2014 Pengaruh jenis non-pelarut dan penambahan polimer hidroflik terhadap struktur morfologi membran poliersulfon Prosiding Seminar Nasional Aplikasi Sains & Teknologi (SNAST) (Yogyakarta, 15 November 2014) 249
[7] Fauzzia M, Rahmawati I and Widiasta I N 2013 J. Teknol. Kim. dan Ind. 2 155
[8] Arahman N 2014 Int. J. Appl. Eng. Res. 9 10453-62
[9] Ghaemi N, Daraei P and Akhlaghi F S 2018 Carbohydr. Polym. 191 142
[10] Bagheripour E, Mohgadassi A R, Hosseini S M, Van der Bruggen B and Parvizian F, 2018 J. Ind. Eng. Chem. 62 311
[11] Dong C, He G, Li H, Zhao R, Han Y and Deng Y 2012 J. Memb. Sci. 387 40
[12] Jochym P T, Oleś A M, Parlinski K, Łazewski J, Piekarz P and Sternik M 2010 IOP Conf. Ser.: J. Phys. Condens. Matter. 22 1
[13] Mulder M 1991 Basic Principles of Membrane Technology 1st ed. vol 53 (USA: Kluwer
[14] Coates J 2000 Encyclopedia of Analytical Chemistry (Chichester: John Wiley & Sons Ltd) 10815
[15] GuoW, Chen J, Sun S and Zhou Q 2018 J. Mol. Struct. 1171 600
[16] Yuan S, Li J, Zhu J, Volodine A, Li J, Zhang G, Puyvelde P V and Bruggen B V 2018 J. Memb. Sci. 563 655
[17] Aprilia S and Arahman N 2016 Mns. dan Lingkung. 23 149
[18] Han S, Mao L, Wu T and Wang H 2016 J. Memb. Sci. 516 47
[19] Farahani M H D A, Rabiee H and Vatanpour V 2019 J. Water Process Eng. 27 47
[20] Kusumawati N and Tania S 2012 Molekul. 7 43
[21] Zhao Q, Xie R, Luo F, Faraj Y, Liu Z, Ju X J, Wang W and Chu L Y 2018 J. Memb. Sci. 549 151
[22] Mulyati S, Razi F and Zuhra 2017 Biopropal Ind. 8 55