# The Improvement of Hydrophilic Property of Polyethersulfone Membrane with Chitosan as Additive

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**Abstract**

Membrane technology has been implemented broadly for clean water treatment. To produce a better membrane, modification is carried out by adding chitosan into polymer solution. Materials used in this research are polyethersulfone (PES) 18%, the n-methyl pyrrolidone solvent modified with a chitosan solution (at 0.2 – 1 wt%) as an additive, and deionized water as a non-solvent. The membrane synthesis is carried out with the non-solvent induced phase separation method of blending the polymer. Membrane characterization includes functional group analysis, morphological structure, and water contact angle. Membrane performance is monitored at the filtration process, resulting in the permeability coefficient, and for the rejection of a contaminant (humic acid) with dead-end filtration. Research results show that the modified membrane characterization has an asymmetric morphological structure with a thinner top layer, and the membrane sublayer has a finger-like macrovoid structure with a larger size as compared to the original PES membrane (without the chitosan solution addition). The chitosan additive into the PES membrane improves the membrane's hydrophilic property. The highest value of the permeability coefficient is achieved with 1% chitosan addition, which provides a permeability coefficient value of 11.2 L/m$^2$.h.bar and a rejection coefficient of 70.3%.

Keywords: membrane, chitosan solution, polyethersulfone, hydrophilic property, ultrafiltration.

## 1. Introduction

Apart from oxygen, water is the most basic needs of human beings. Up to 60% of the adult human body consists of water. Safe access to clean drinking water is essential to survival. The earth consists of only 3% fresh water with only 0.01% accessible for human use. Ongoing increases in urbanization and population growth can no longer be sustained with such a small amount of clean, accessible water (Munnawar et al., 2017).

In recent years, membrane use has expanded and improved globally for treating clean water and waste water. Separation membranes have been implemented broadly as a substitute for the conventional system of water treatment (Mohammad et al., 2015; Su et al., 2014). Contaminant element separation from potable water with membrane technology has developed rapidly (Fahrina et al., 2018).

One of the popular polymer materials used in the membrane synthesis industry is PES. PES is trendy because of its thermal and chemical stability and its excellent mechanical property (Yu et al., 2013). In addition, PES has sufficient pH tolerance and endurance toward chlorine with a glass transition temperature (Tg) of 230°C (Mulder, M., 1991). However, PES membrane also has a weakness. Fouling forms easily because of the hydrophobic property of a PES membrane. The research result for the water contact angle of a pure PES membrane is 88.6° (Wang et al., 2014), which shows that PES is quite hydrophobic. Significant research has been carried out to improve the hydrophilic and anti-fouling properties of the polymer membrane, such as modification with other polymers through polymer blending with a third compound (Liu et al., 2014; Arahman., 2015), chemical grafting (Luo et al., 2015; Huang et al., 2015), and surface modification (Zhou et al., 2008)

Chitosan is a hydrophilic polymer commonly used to modify a hydrophobic membrane, such as polyvinylidene fluoride (PVDF), poly-acrylonitrile (PAN), and PES with the goal of improving the membrane's hydrophilic property. Chitosan, a polysaccharide biopolymer with a significant content of hydroxyl and amine functional groups, is the most applicable and useful chitin derivative. Chitin is commonly extracted from the second largest biopolymer with adsorptive capability, Crustaceans shell (Lakra et al., 2013; Salehi et al., 2016). Its high hydrophobic property, good biocompatibility, non-toxic property, low cost, and renewability as a natural resource are interesting benefits of chitosan as a naturally-formed biopolymer (Elizalde et al., 2018; Pillai et al., 2009). Because of these highly advantageous characteristics, chitosan has been used in wastewater treatment, adsorption of heavy metal ions from water, membrane biomaterials, pharmaceuticals, and nutraceuticals.

Chitosan also can improve the mechanical properties of polymers (Salehi et al., 2016). Besides, amino and hydroxyl groups in chitosan can be used as absorbents for various dyes, macromolecules and heavy metals (Kumar et al., 2000; Rinaudo., 2006; Serizawa et al., 2002). The combination of chitosan with suitable polymers such as silica, graphene oxide, and polyvinyl alcohol can produce highly reactive reactions and the stability of the mechanical properties of membranes (Seo et al., 2014; Shao et al., 2013; Shawky., 2009). Polyvinyl alcohol (PVA) is very hydrophilic and is compatible with chitosan polymers, and has also been widely used to improve the mechanical and chemical properties of chitosan membranes (Liu and Bai., 2006; Jin and Bai., 2002).

Some researchers modified the chitosan membrane for application in dyes removal in water. Preparation of Thin Film Composite (TFC) membranes have been done by Daraei et al, which is applied to remove the methylene blue in water, wherein the chitosan nanocomposites coated on the microfiltration PVDF membrane (Daraei, et al., 2013). This prepared membrane was used to remove dyes in water, which has also been studied by Karim et al (Karim et al., 2014). And in other studies, nanocomposite membranes are fabricated by modifying chitosan with montmorillonite (He et al., 2016). In addition to removing several dyes

in water, chitosan membranes can also be applied to remove heavy metals in water (Kamiński and Modrzejewska., 2013).

In this study, membrane modification was investigated with chitosan as an additive in a PES membrane. Chitosan was added as a pore-forming agent to increase the hydrophilic property of the PES membrane. The membrane synthesis was performed by phase inversion through non-solvent induced phase separation (NIPS) with modification by polymer blending. Fabricated membranes were used to remove organic compounds in water, where humic acid was used as a model foulant for Nature Organic Matter (NOM). Membrane characterization and the performance of the modified membrane were investigated.

## 2. Methodology

### 2.1. Materials

PES (Ultrason E6020) served as the polymer for membrane synthesis. It had a molecular weight of 65000 was purchase from the BASF Co. NMP from Merck was used as a solvent, and chitosan (Sigma aldrich, Germany) was used as an additive. The other materials were *deionized water,* used as a non-solvent; a humic acid solution, used as an artificial sample for contaminated water; and a set of dead-end filtration equipment.

### 2.2. Synthesis of Chitosan Solution

Chitosan was ground using a ball mill for 20 hours. Ground chitosan was then screened with a vibrating screen with a 325-mesh sieve. To synthesize the chitosan solution, one gram of chitosan was dissolved in 100 mL of acetic acid 1% (Munnawar et al. 2017). Next, agitation was carried out until the solution was homogeneous for 24 hours. The derived chitosan solution was kept at room temperature for use as an additive in the synthesis of the modified PES membrane. Concentration of 0.2 wt% (K-1), 0.6 wt% (K-2), and 1 wt% (K-3) were prepared.

### 2.3. Synthesis of Membrane

A flat membrane was made through nonsolvent induced phase separation, as described here. The PES polymer was dissolved into the NMP solvent to create the dope solution. This PES

concentration was made fixed at 18% wt. The chitosan solution addition was carried out at 0.2 wt%, 0.6 wt%, and 1 wt%. Then, each dope solution was stirred with a stirrer until homogeneous. Each homogeneous dope solution was placed into sonicator for 30 minutes to avoid chitosan agglomeration. Next, each dope solution was cast; it was poured onto a glass plate (casting process) and then flattened onto the entire surface of the glass plate with a casting knife at 300 µm thickness. The glass plate was then dipped into a coagulation bath containing deionized water. In this step, the membrane solidification process occurred, which changed the polymer from its liquid phase into its solid phase. All membranes fabrication process was carried out at room temperature (27°C) with humidity 61%. Then, each membrane was left in the deionized water before it was used for the filtration test and membrane characterization (Table 1).

**Table 1**. Compositions of dope membrane solution

| No | PES (%) | Chitosan Solution (%) | NMP (%) | Membrane |
|----|---------|-----------------------|---------|----------|
| 1 | 18 | 0.0 | 82.0 | K-0 |
| 2 | 18 | 0.2 | 81.8 | K-1 |
| 3 | 18 | 0.6 | 81.4 | K-2 |
| 4 | 18 | 1.0 | 81.0 | K-3 |

## 2.4. Membrane Characterization

Membrane characterization was carried out by observing the membrane morphology (cross section membrane) using Field-Emission Scanning Electron Microscopy (FE-SEM; JSF-7500F, Jeol Co.,Ltd., Tokyo, Japan), analyzing the functional group composition of the membrane using Fourier Transform Infrared (FTIR-ATR, Thermo Scientific iD5 ATR-Nicolet iS5 FTIR Spectrophotometer, Shimadzu, Japan), and measuring hydrophilic property of the membrane using the contact angle meter (Drop Master 300, Kyowa Interface Science Co., Saitama, Japan).

## 2.5. Performances of Pure Water Permeation and Rejection Coefficient of Membrane

Membrane performance was monitored for filtration process, namely the permeability coefficient, and rejection of the humic acid solution using module dead-end filtration. The

feed was put into feed intake holes towards the membrane surface. Then, inert gas of nitrogen was channelized as a feed driving force through membrane media originating from a nitrogen gas tube with an operating pressure of 1; 1.5; 2; and 2.5 bars. Furthermore, permeate was collected and the permeate-flow rate was measured by recording the volume stored at an interval of 10 minutes until it reaches a constant volume. Then, both flux and permeability coefficient were calculated. This flux of membrane was obtained from the change of permeate volume per unit of time and membrane surface area. The equation used to calculate flux (J) (Mulder, M., 1991) was:

$$J = \frac{1}{A}\frac{dV}{dt} \tag{1}$$

Where,
A  = surface area ($m^2$)
dV  = permeate volume (L)
dt  = permeation time (hour)

This membrane permeability coefficient showed the easiness of feed to pass the membrane. The equation used to calculate the membrane permeability coefficient ($L_p$) (Mulder, M., 1991) is:

$$L_p = \frac{J}{\Delta_p} \tag{2}$$

Where,
J  = water flux ($L/m^2 \cdot jam$)
$\Delta p$ = pressure drop (atm)

The rejection coefficient was a concentration fraction of a solute that did not penetrate the membrane. This equation of the rejection coefficient (R) (Mulder M., 1991) is:

$$R = 1 - \frac{Cp}{Cf} \times 100\% \tag{3}$$

Where,
R  = Rejection coefficient (%)
Cp  = Solute concentration in permeate (mg)
Cf  = Solute concentration in feed (mg)

Rejection coefficient of humic acid was measured by channelizing humic acid solution into dead-end filtration membrane at a pressure of one bar for one hour and every 10 minutes, permeate was weighed. This humic acid solution

was made by dissolving 50 mg of humic acid solid into one liter of deionized water. Furthermore, the solution was agitated for 24 hours until completely dissolved. This humic acid solution was used as a sample for membrane rejection test.

## 3. Results and Discussions

### 3.1. Functional Group Analysis

FTIR Spectroscopy is an instrument commonly used to know the functional group of a sample surface based on the molecular interaction presence, such as absorbance or transmittance from infra-red (IR) light provided with the sample. IR spectrum of various types of membrane appears in Figure 1.
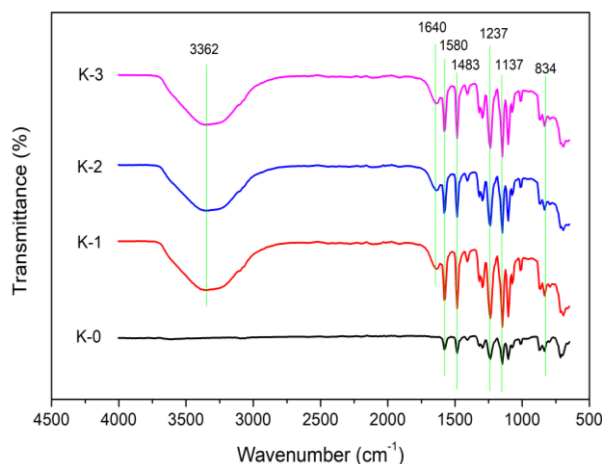


**Figure 1**. IR spectrum at various types of membrane.

Generally, at spectrum shown in Figure 1, original PES membrane (K-0) and modified PES membrane (K-1, K-2, and K-3) appears to have an almost similar spectrum structure with chitosan solution added. The group of aromatic chain (C=C) can be seen in the FTIR spectrum at all membranes at wavenumber of 1483 and 1580 $cm^{-1}$. The sulfonic group (O=S=O) was detected at the peak of wave number 1137 $cm^{-1}$, aromatic ether group (C-O-C) with wave number of 1237 $cm^{-1}$ and aromatic C-H group at wave number of 834 $cm^{-1}$. All peaks of the emerged wave number relate to atom vibration in material characterizing the polyethersulfone (PES) presence.

The peak that appears at a wavenumber of 3362 $cm^{-1}$ on the K-1, K-2, and K-3 membranes is related to the hydroxyl (OH) group stretching vibrations and the primary amine (NH) (asymmetrical strain) group that present on the PES modified membrane. Whereas the small peak that appears at a wavenumber of 1640 $cm^{-1}$ indicate the N-H group of the secondary amine group (symmetrical strain) (Haldorai and Shim, 2014; Shakeri et al., 2017). This indicates the presence of chitosan chains in the membrane material. Thus in this research, it was stated that chitosan was successfully added to the PES polymer by polymer blending technique.

### 3.2. Membrane Morphological Structure

The membrane morphological structure is tested using *Scanning Electron Microscopy* (SEM). SEM test is represented for a membrane with the highest permeability coefficient, namely K-3 membrane (PES with 1% chitosan solution addition) and the lowest one, namely K-0 membrane (original PES). Morphological structure of cross section membrane with various magnification can be seen in Figure 2 (for K-0 and K-3 membrane).

Figure 2 show the morphological structure of a cross-section for K-0 membrane (original PES) and K-3 membrane (PES membrane modified with 1% chitosan solution addition). In Figures of (A)–(D) all membranes appear in the asymmetric form with a dense layer is available as active layer and sub layer as membrane support. The structure of finger like macrovoid is clearly formed on the sub-layer of both membranes. This is a usual form of membrane formed by NIPS method. The morphological structure difference of K-0 membrane (original PES) and K-3 membrane (membrane modified with 1% chitosan solution addition) can be seen from the figure. The difference can be seen in a thinner dense layer of K-3 membrane (Figure 2B) compared to that of K-0 membrane (Figure 2A).

The other difference also can be seen in the macrovoid structure of sub-layers of both membranes. In K-3 membrane, the amount of macrovoid appears more compared to that of original PES membrane (K-0 membrane). The macrovoid size of the K-3 membrane (Figure 2D) also can be seen larger compared to that K-

0 membrane (Figure 2C). The increase of macrovoid amount presence is presumably because of the presence of some additives coming out of the polymer system during the coagulation process in a coagulating bath consisting non-solvent liquid *(deionized water).* It occurs because of the presence of the irregularity of bonds among polymers, solvents, and additives during membrane synthesis process (Rahman et al., 2008).
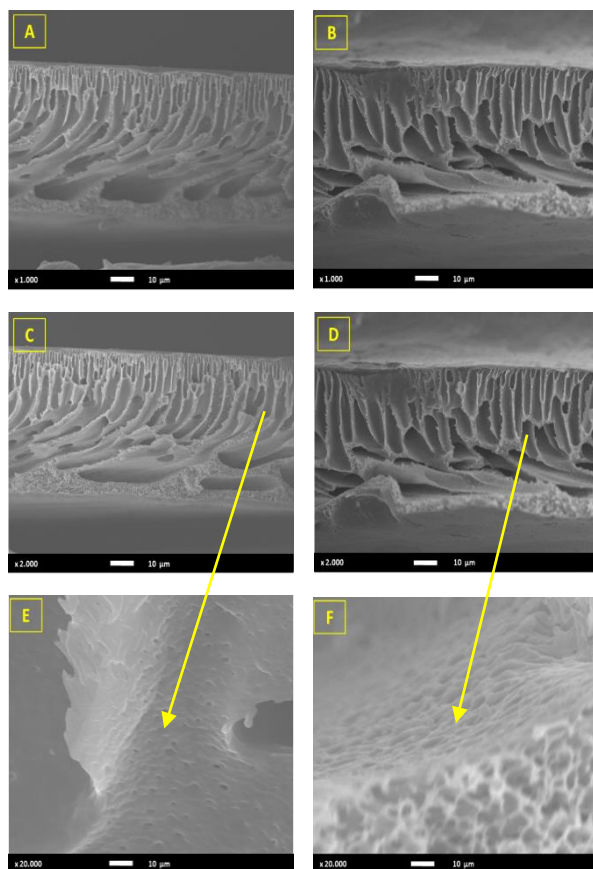


**Figure 2.** Morphological structure of K-0 membrane (A, C, and E) and K-3 membrane (B, D, and F). (A) and (B) 1000 times of magnification; (C) and (D) 2000 times of magnification; (E) and (F) 20,000 times of magnification at macrovoid section.

In this matter, the chitosan solution addition has an impact on decreasing the number of non-solvents needed during the separation phase process. This is presumably the reason for the increase in the number of macrovoid formed in the membrane modified with the chitosan addition (K-3). Furthermore, the

difference in pore size, and pore distribution in the membrane can be seen in Figures of 2E and 2F. The more pores and the larger pore size appear in the K-3 membrane (Figure 2F) compared to K-0 membrane (Figure 2E). Likewise, pore distribution in K-3 looks more evenly distributed in the macrovoid wall compared to K-0 membrane (original PES).

It indicates that the presence of hydrophilic additive particles in the casting solution increases the rate of exchange of solvents-nonsolvents during the phase inversion process that affects changes in pore structure and thickness of the top layer (Zheng et al., 2004). From Fig. 2, it can be observed how the pore size of the membrane increases with the addition of chitosan. In addition, cross-sectional images depict an asymmetrical structure in which the addition of chitosan creates wider channels in the finger-like layers, but without significant changes in the increase in chitosan concentrations exceeding 1.0%. This structural change can be ascribed to the intrusion of large amounts of non-solvent (water) into the cast film because the concentration of hydrophilic chitosan particles increases, resulting in larger pores. Likewise, as chitosan concentration increases, the membrane pore size also increases (Elizalde et al., 2018).

### 3.3. Water Contact Angle

Permeability and anti-fouling is membrane performance parameter influenced by hydrophilic property of the membrane. This hydrophilic property of the membrane can be investigated by measuring water contact angle. The membrane is said as hydrophobic if water droplets do not spread on the membrane surface with contact angle above or close to $90^O$. Whereas a membrane with high hydrophilic level has a contact angle below $90^O$, because of the water droplets given can be adsorbed on the membrane surface (Jhaveri and Murthy, 2016). The lower the value of water contact angle, thus the more hydrophilic the membrane (Ghaemi et al., 2018). The resulted hydrophilic membrane can be seen in Figure 3.

Figure 3 shows that K-0, K-1, K-2, and K-3 membrane have contact angle values of 84.2°, 76.6°, 72.5°, and 71.1°, respectively. It shows that the original PES membrane (K-0) has hydrophobic property, whereas K-1, K-2, and K-

3 membranes can be said more hydrophilic compared to K-0 membrane. The addition of chitosan solution as additive in the membrane provides an increase in the hydrophilic properties of the membrane, namely by the PES polymer presence with chitosan confirmed by the characterization of the membrane functional group using FTIR (Figure 1).
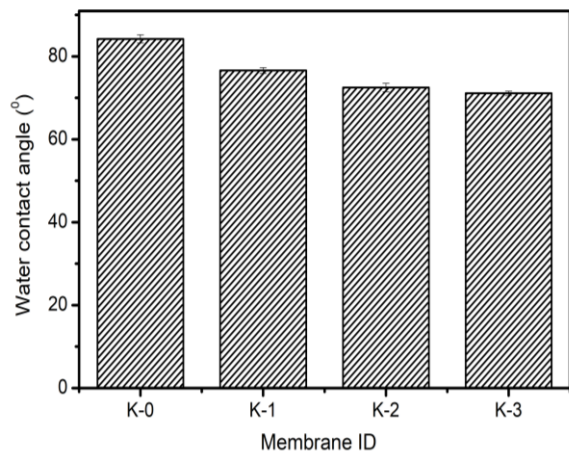


**Figure 3**. Water contact angle at various types of membrane.

The presence of hydrophilic hydroxyl group (-OH) in a chitosan can make the hydrophobic membrane (K-0) become more hydrophilic as seen in modified membranes identified by the occurrence of a decrease in membrane water contact angle. This same result is also stated by previous researchers (Boributh et al., 2009) stating that an increase of chitosan concentration can increase hydrophilic property of the membrane (a decrease of water contact angle).

**3.4. Permeability Coefficient**

The important parameter of membrane performance is water permeability or flux and solute rejection or ability to reject particle in a particular solution. Water permeability is the amount of water volume filtered through the membrane layer per unit of membrane surface area, filtering time, and operating time. Figure 5 shows water permeability profile in the original PES membrane (K-0) and K-0 membrane modified with the chitosan solution addition at various concentrations of 0.2, 0.6 and 1 wt%. (K-1, K-2, and K-3). Based on the figure, K-0

membrane appears to have the lowest water permeability compared to K-1, K-2, and K-3 membrane. This phenomenon is related to the change of membrane morphological structure as seen in Figure 2. A top layer (dense layer) in K-0 membrane is thicker compared to modified membrane (K-3 membrane). This thick top layer inhibits the particle separation contained in the sample solution that solution permeability obtained becomes lower compared to PES membrane modified with chitosan solution addition (K-1, K-2, and K-3). The thickness of the top layer (dense layer) makes macrovoid structure in the membrane narrows, reduce the number, and pore distribution in the membrane that solution permeability becomes low.
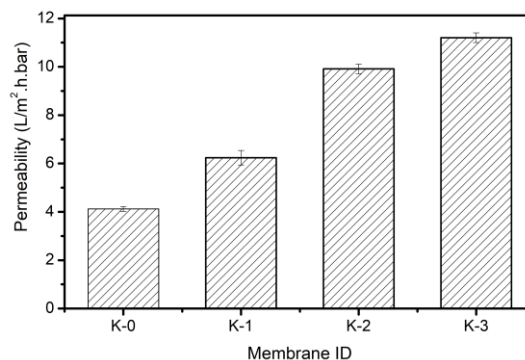


**Figure 4.** Permeability of pure water (Lp) at various types of membrane.

The increase in water permeability in the membrane modified with the chitosan solution addition (K-1, K-2, and K-3) also can be observed with the hydroxyl group (-OH) presence from chitosan confirmed from functional group analysis using FTIR in Figure 1. This hydroxyl group (-OH) presence in a chitosan with hydrophilic property can increase hydrophilic property of K-1, K-2, and K-3 membranes. Hydrophilic property is an important parameter in the membrane because it increases the water molecule interaction with membrane surface to affect a water permeability performance that also simultaneously reduces the interaction with foulant leading to the best anti-fouling property. An increase of water permeability in the membrane modified with chitosan addition is 6.2 L/m$^2$.h.bar for K-1 membrane, 9.9 L/m$^2$.h.bar for K-2 membrane, and in K-3 membrane is 11.2 L/m$^2$.h.bar.

Membrane water permeability is also influenced by the value of a membrane water contact angle*.* An increase of water permeability in these K-1, K-2, and K-3 membranes can be understood from the measurement of water contact angle in Figure 3. In the water contact angle measurement, K-1, K-2, and K-3 membranes are found to have higher hydrophilic property compared to original PES membrane (K-0). An increase of this hydrophilic property affects the permeability value of the membrane resulted. It can be stated that a decrease of water contact angle (an increase of hydrophilic property) is able to increase the membrane permeability coefficient.

## 3.5. Humic Acid Rejection

The membrane performance test is also carried out by rejection test using humic acid as an artificial sample to see membrane performance in removing natural organic compounds in water. Humic acid refers to the humic substance fraction contained in soil and emerges in the water surface at low concentration as decomposition products of lignin, carbohydrate, and protein (Ruohomtiki and Kaipia, 1996). The rejection coefficient of a humic acid particle at various types of membrane can be seen in Figure 5.
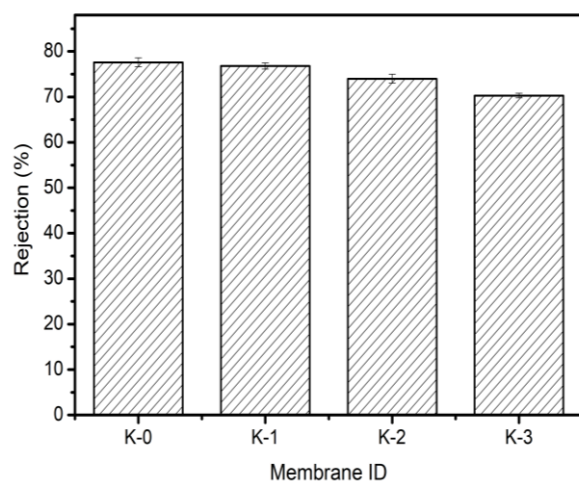


**Figure 5.** Rejection of humic acid solution at various types of membrane.

Figure 5 shows that K-0 membrane has the highest rejection coefficient, namely 77.6%. The membrane rejection coefficient gets decreased by the membrane presence modified with chitosan solution addition, namely in K-1, K-2,

and K-3 membranes at 76.8%, 74%, and 70.3%, respectively. Rejection coefficient in original K-0 membrane is higher compared to K-1, K-2, and K-3 membranes, K-0 membrane (Figure 2E) presumably has a smaller pore size compared to K-3 membrane (2F). A smaller pore size causes K-0 membrane more selective for solution passing the membrane compared to the membrane modified with chitosan solution addition (K-1, K-2, and K-3). The same result is also obtained by previous researchers by modifying PES/chitosan (Ghaee et al., 2013) with performance of copper metal rejection of 76%. The membrane modification with chitosan addition can be stated as promising for industrially waste water treatment.

## 4. Conclusion

Characterization and performance test of PES membrane modified by adding chitosan has been conducted. The characterization result shows that the interaction presence between PES polymer and chitosan from analysis using FTIR with the hydroxyl group (OH) presence from chitosan causes membrane hydrophilic property increased. The increase of this hydrophilic property can be confirmed with a decrease of water contact angle in the membrane modified with chitosan membrane. Characterization using SEM shows that membrane modified with chitosan solution has an asymmetric form with a top layer has a thinner dense layer, whereas a bottom layer (support) has a form of finger like macrovoid, with numbers of more pores and larger size compared to original PES membrane. Modified membrane performance provides permeability coefficient value of 11.2 L/m$^2$·h·bar and rejection coefficient of 70.3%.

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