Improving Hydrophilicity of Polyethersulfone Membrane Using Silver Nanoparticles for Humic Substances Removal


Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, Cheras, Kajang, Selangor, Malaysia

**ABSTRACT**

Silver-impregnated membrane was facilely prepared by ex situ silver nanoparticles (NPs) blending method using polyethersulfone (PES) as the base polymer. A total of three membranes [F1(S0), F2(S0.5) and F3(S2.0)] were fabricated at different weight percentages of polymer and silver (Ag) loadings to compare their effects on membrane morphological and performance properties. All membrane types were characterized using scanning electron microscope (SEM), energy-dispersive X-ray, zeta potential analyzer and contact angle analysis. Characterization data and background theories from the literature were used to study and relate the effect of silver nanoparticles (AgNPs) on the physicochemical properties of the PES/Ag composite membranes with respect to pure water permeability, structural property, surface charge and surface hydrophilicity. Solute rejection performance and antibacterial property of the PES/Ag composite membranes were performed using humic acid (HA) and Escherichia coli bacteria. The results showed that the membrane with the highest Ag loading (F3) exhibited the highest pure water permeability among all the composite membranes. This phenomenon could be attributed to the morphological changes of the membrane due to addition of Ag. In this study, contact angle of the membranes showed decreasing trend with addition of Ag as well as increase in Ag loading. On the contrary, pore radius of the membranes was found increased with increasing in Ag loading. Owing to this, the F3 membrane demonstrated relatively lower HA rejection (i.e. 89.55%) compared to pure PES membrane. In terms of the antibacterial performance evaluation, one can confidently state that the membranes with addition of Ag showed excellent property in biofouling mitigation based on numerous dead E. coli observed on the membrane surface under SEM analysis.

**Keywords**

Antibacterial, E. coli, Hydrophilicity, Polyethersulfone, Silver Nanoparticle

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**NOMENCLATURE**

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<th>Description</th>
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<td>A</td>
<td>Effective membrane area in m²</td>
</tr>
<tr>
<td>C₀</td>
<td>Concentration of HA in feed in ppm</td>
</tr>
<tr>
<td>Cᵢ</td>
<td>Concentration of HA in permeate in ppm</td>
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<tr>
<td>Lₚ or PWP</td>
<td>Pure water permeability in LMH/bar</td>
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<td>l</td>
<td>Thickness of membrane in metre (m)</td>
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<tr>
<td>ΔP</td>
<td>Transmembrane pressure difference in Pascal (Pa) / bar</td>
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<tr>
<td>Q</td>
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<td>Rᵢ (%)</td>
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<td>Wₗ</td>
<td>Weight of dried membrane in gram (g)</td>
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**Greek Symbols**

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<tr>
<td>ε</td>
<td>Membrane porosity</td>
</tr>
<tr>
<td>η</td>
<td>Viscosity of pure water in kg.m/s</td>
</tr>
<tr>
<td>ρₘembrane</td>
<td>Density of membrane in kg/m³</td>
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<td>ρₜₜₜₜₜₜₜ</td>
<td>Density of water in kg/m³</td>
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1. INTRODUCTION

Membrane technology is an emerging separation process. It possesses the advantages of easy operation, high productivity in terms of permeate and flux, does not require additional chemicals, and minimum space requirement. Among others, phase inversion is the most commonly used membrane fabrication technique in both laboratory scale and commercial industry. Meanwhile, polyethersulfone (PES) has been affirmed as one of the important polymeric membrane materials owing to its desirable properties such as low cost, high chemical
resistance, wide pH tolerance, good chlorine resistance, good miscibility with additives and solvents [1]. However, membrane filtration usually encounters problems like low permeation flux and inefficient separation performance due to surface hydrophobicity property of the membrane material. As reported in literature, membrane surface properties such as hydrophilicity, surface charges and roughness have great impacts on membrane fouling [2]. Hence, developing a membrane with excellent surface hydrophilicity and outstanding antifouling performance is very crucial to ensure the practicability of membrane.

Humic substances are the predominant species of dissolved natural organic matter (NOM) which can be categorised into humic acid (HA), fulvic acid and humin based on their solubility at different solution pH values [3]. In general, HA possesses three main functional groups, i.e. carboxylic, phenolic alcohols and methoxyl carbonyls group. The reaction between HA and other organic compounds may lead to the formation of chlorinated by-products such as trihalomethane and haloacetic acid which are known to be carcinogenic [4]. Since HA is the major component species in NOM, it was widely used as a model organic material in numerous studies [5, 6]. On the other hand, filtration of bacteria-containing wastewater would induce biofouling, which further deteriorates membrane separation performance, resulting in higher operation pressure and so does the operation cost. Biofouling begins with bacteria adhesion on membrane surface, in which bacteria produce a biofilm containing polysaccharide, organic substance and complex community of microbial cells [7]. This layer is difficult to be removed and induces irreversible damage to the membrane.

It was commonly reported in the literature that impregnation of additives such as alumina, ferric oxide, titanium dioxide and silver into membrane matrix could affect its morphology as well as membrane performance [6, 8, 9]. Ananth and co-workers [10] also reported that tear-shaped porous membrane was formed when silver nanoparticles (AgNPs) were incorporated into PES membrane. Furthermore, Basri, Ismail and Aziz [8] revealed that membrane porosity increased with a higher silver loading in the membrane. In contrary, some researchers claimed that higher silver content would lead to smaller membrane pores, resulting in a higher rejection but lower flux [11]. Leaching of silver during phase inversion is a major factor that affecting the formation of membrane pores, including the shape, size and number of pores present. Besides, several factors including type of solvent, particle size of silver and type of polymer might greatly influence the rate of solvent exchange, hence give rise to an inconsistency of findings in the literature.

On the other hand, there are numerous studies claiming that incorporating silver NPs into membrane matrix could promote anti-biofouling and antibacterial properties. This is because silver NPs provide toxic effect upon its contact with bacteria cell membrane, for which silver ions bind to sulphur group and destabilized protein of bacteria cell [12]. Direct contact between bacteria and silver on membrane surface could facilitate silver ions uptake by bacteria cells and this would offer some contributions to bactericidal effect [13]. Direct interaction of bacterial cell and silver NPs lead to the formation of holes and pits on cellular surface, thus induced the leakage of cytoplasmatic material and loss of morphological integrity [14]. Literature also reported that silver NPs can destroy cell wall easily, thus it is effectively against aquatic microorganism such as fungi, bacteria and algae [15].

Other than silver NPs, polyvinylpyrrolidone (PVP) with molecular weight (MW) ranged from 10 to 360 kDa are widely used as modifiers. They are usually either coated on membrane surface or added into casting solution [8]. The authors also reported that long chain PVP with high molecular weight yields optimum silver capping in the fabrication of Ag/PES composite membrane. Literature also reported that weight ratio of silver NPs to PVP should be kept at 1:1 for better silver distribution in the membrane matrix [8, 13]. As reported by Lee and co-workers, silver NPs had been observed in such behaviour that greatly improved dispersion rate with the same composition of PVP to silver NPs [16]. Other than improving membrane hydrophilicity, PVP also plays a vital role in Ag-capping owing to its chemical structure. The nitrogen atom in PVP prevents silver NPs from growing and agglomeration [17]. The combination of polymer and silver NPs gave rise to polymer-hosting, whereby polymer offered protection to silver NPs from detachment or leaching [18]. The leaching of silver is responsible for the formation of larger pores during phase inversion, thus adding PVP into the membrane could stabilize silver NPs in the polymeric membrane matrix and suppress the formation of macrovoid [8].

As mentioned earlier, incorporation of antimicrobial silver NPs into membrane matrix would offer an innovative potential solution to prevent biofouling as well as to improve membrane performance in terms of removing hazardous microbes from the feed [19]. Numerous studies have reported the impregnation of silver NPs in different types of polymeric membrane, including PES [8, 10], cellulose acetate, polysulphone [19, 20], polyamide, polyimide and polyvinylidene fluoride [7]. However, studies related to humic substances removal using PES membrane impregnated with silver NPs are rarely reported. Thus, there is a lack of understanding on how the changes in membrane morphologies and structural properties affecting HA removal. Hence, this study was initiated to investigate the performance of PES/Ag membrane in terms of pure water flux, HA solutes rejection and antibacterial properties.
2. EXPERIMENTAL

2.1. Materials Polyethersulfone (PES granule, MW = 35,000 g/mol, Solvay, UK) was chosen as the base polymeric material to synthesize the PES/Ag membrane. Meanwhile, N-methylpyrrolidinone (NMP, 99.5%, Merck, Germany) was selected as solvent to dissolve PES polymer. Nanosized silver nanoparticles (particle size ≤ 100 nm, 5 wt% in ethylene glycol, Sigma-Aldrich, USA) and polyvinylpyrrolidone (PVP, MW = 29,000 g/mol, Sigma-Aldrich, Germany), were added to promote antibacterial property and to control membrane pore size, respectively. Humic acid (powder, 4710 g/mol, Sigma-Aldrich, Switzerland) was used as the solution model for membrane solute rejection studies while sodium bicarbonate (99%, Chemsoln, Malaysia) was added to improve humic acid solubility in water. The distilled water used in this study was obtained from a laboratory distillation unit (Favorit W4L Water Stills, Malaysia). All reagents were of analytical grade and used as received.

2.2. Membrane Fabrication Table 1 summarizes the dope compositions of flat sheet membranes. Prior to the preparation of the membrane dope solution, PES and PVP were dried in an oven at 60 °C overnight to remove the moisture contents from the polymers. Dope solution of F1 was prepared by dissolving 15 wt% of PES into 85 wt% of NMP solvent under continuous stirring at 60 °C for 4 h in order to form a homogenous dope solution. To prepare dope solution of F2 and F3 membranes, the compositions of PES, PVP, AgNPs and NMP were adjusted according to the dope composition tabulated in Table 1.

Firstly, the casting solutions were prepared by dissolving different amount of AgNPs (0.5 wt% and 2.0 wt%) into NMP solvent. The dispersion process of AgNPs: PVP were dried in an oven at 60 °C. Subsequently, PVP powder was then added into the casting solution. Upon complete dissolution of PVP, AgNPs and NMP, the exchange of solvent was carried out. The casting solution was poured on a smooth glass plate. The distilled solution formed was cooled for 30 min before it was stirred continuously. Upon complete dissolution of PVP, AgNPs and NMP the membrane was formed on the glass plate via phase inversion process. The membrane was then being transferred to another distilled water bath and stored wet at room temperature overnight to remove residual solvent.

The membrane was casted with a thickness of 250 μm using adjustable film applicator (Braive Instrument, Germany). The wet polymeric film was left for evaporation for 30 s to allow the formation of thin film before it was immersed into distilled water bath at room temperature [1]. Subsequently, the exchange of solvent and non-solvent (water) took place and a flat sheet polymeric membrane was formed on the glass plate via phase inversion process. The membrane was then being transferred to another distilled water bath and stored wet at room temperature overnight to remove residual solvent.

2.3. Membrane Characterization and Performance Testing The hydrophilicity of the fabricated membranes surface were determined by sessile drop method using Easy Drop contact angle goniometer (KRUSS GmbH, Germany) conducted at room temperature. Approximately 1 μL droplet of distilled water was carefully dropped on the top surface of membrane specimen and the contact angle was measured immediately after the drop placement. Five measurements were obtained on each membrane specimen at different locations and the values were averaged to acquire a reliable value.

A dead-end filtration cell (Sterlitech™ HP4750) with an active membrane area of 14.6 cm² was adopted to evaluate the permeation flux of the fabricated membranes. The fabricated membranes were cut into circular membrane coupon of 49 mm in diameter and then pressurized under compaction of 12 bar for 2 h prior to pure water permeability (PWP) test at 10 bar.

Pure water permeability (PWP or \(L_p\)) was calculated using Equation (1).

\[
L_p = \frac{\Delta q}{A \times \Delta t \times \Delta P}
\]  

where \(L_p\) is in LMH/bar, \(Q\) is the volume of permeate in litre (L), \(A\) is the effective membrane area (m²), \(\Delta t\) is the time taken to collect the permeate (hour) and \(\Delta P\) is the transmembrane pressure difference in bar.

The membrane porosity (\(\varepsilon\)) was calculated using Equation (2) [21].

\[
\varepsilon = \left(\frac{W_1 - W_2}{W_1/\rho_{water} \times W_1/\rho_{membrane}}\right) \times 100\%
\]  

where \(W_1\) represents the weight of wet membrane, measured using analytical balance after immersing it into distilled water for 4 h. \(W_2\) represents the weight of dry state membrane, obtained after drying overnight in oven at 60 °C. Both \(W_1\) and \(W_2\) are in unit kg. \(\rho_{water}\) and \(\rho_{membrane}\) are the density of water and membrane in dry state, respectively. The pore radius \(r_m\) of the membrane was calculated using Equation (3) [21].

\[
r_m = \sqrt{\frac{(29.8 - 1.75 \varepsilon) \times 8 \times n \times q}{\varepsilon \times A \times \Delta P}}
\]  

\(\Delta P\) is the transmembrane pressure difference in bar.\(\Delta q\) is the permeate flux in L/m²h.\(A\) is the effective membrane area in m². \(\varepsilon\) is the membrane porosity. \(n\) is the number of pores per unit area. \(\Delta t\) is the time taken to collect the permeate (hour). \(\rho_{water}\) and \(\rho_{membrane}\) are the density of water and membrane in dry state, respectively.
where \( l \) is the thickness of the membrane (m). \( \eta \) represents the viscosity of pure water in kg m/s, whereas \( \Delta P \) is the transmembrane pressure in Pa.

The surface charges of membranes were measured using a zeta potential analyzer (Malvern Instruments Nano ZS, UK). The zeta potential of membrane surface was measured in 0.1 mM NaCl at pH 7 using 300-350 nm latex particles as the tracer particles (DTS1235 Malvern, UK). Scanning electron microscope (SEM, Hitachi S-3400N, Japan) was employed to study the surface and cross-sectional structure of the fabricated membranes. For cross-sectional analysis, the membranes were fractured in liquid nitrogen and then coated with gold using a sputter coater (Quorum SC7620, UK) prior to SEM analysis. The magnification was fixed at 2000x while the applied voltage was 20 kV. On the other hand, energy-dispersive X-ray spectroscopy (EDX) was used to identify the presence of Ag element in the fabricated membranes. 0.2 g/L of HA solution was prepared by dissolving the HA powder in 0.05 M of sodium bicarbonate solution to enhance its solubility under constant stirring at 60 °C [5, 22]. The HA feed solution of 10 ppm was fed into the dead-end filtration cell to perform the solute rejection test. UV-visible spectrophotometer (PG Instrument, T60U) was used to measure the UV absorbance of the HA feed and permeate samples at 254 nm [3]. Prior to this, a calibration curve of absorbance against concentration of HA was plotted based on 2, 4, 6, 8 and 10 ppm. With the aids of the calibration curve, the absorbance value can be converted to instantaneous concentration of HA. The HA rejection was subsequently calculated using Equation (4) where \( C_p \) and \( C_f \) represent the concentration of HA in ppm for permeate and feed, respectively [23].

\[
R_{HA}\% = (1 - \frac{C_p}{C_f}) \times 100\%
\]  

(4)

All fabricated membranes were subjected to antibacterial test using disk diffusion method followed by SEM observation. Firstly, the membranes were placed on nutrient agar plates. Then, 10 µL of inoculum contains LB broth nutrient with E. coli at 20 x 10^7 CFU/mL was dropped on each culture plate. Subsequently, the nutrient agar plates were sealed with parafilm and incubated overnight at 37 °C. The growth of E. coli on membrane surface was observed using SEM.

3. RESULTS AND DISCUSSION

3.1. Hydrophilic Study

Table 2 tabulates the contact angles of F1(S0), F2(S0.5) and F3(S2.0) membranes. The contact angle measurements provide crucial understanding on the membrane hydrophilicity. It relies on the concept of interaction between solid membrane surface and liquid, which is defined geometrically as the angle formed by water at three phase boundaries [24]. Water droplet stayed flatten on hydrophilic surface, hence it possessed a lower static water contact angle. Hydrophilic surface has strong water bonding ability which improves the membrane flux for higher productivity by pulling water molecules into membrane matrix and uphold them to the permeate side through the pores [10].

Considering that PES is a hydrophobic material [25], the water contact angle of F1(S0) membrane was found to be as high as 74.73° ± 1.49°. As shown in Table 2, addition of hydrophilic PVP and silver NPs into membrane have resulted in a slight decrement in the contact angles of F2(S0.5) and F3(S2.0) membranes. The results was in agreement with the background theory proposed by Li and co-workers [7], who claimed that silver NPs could enhance membrane surface hydrophilicity. Ngang et al. [26] stated that addition of inorganic NPs into membrane matrix could lead to pore hydrophilization. Inorganic hydrophilic NPs would form a hydroxyl group on membrane surface and pore wall that could attract water molecules to pass through the membrane. Besides, Liu et al. [27] stated that silver NPs could release silver ions in aqueous phase by oxidation, while the released silver ions would be simultaneously adsorbed and deposited on the surface of silver NPs. In fact, the formation of these hydrated silver ions turned out to become the source of silver NPs hydrophilicity [7]. Owing to this, the enhancement in membrane hydrophilicity had improved the permeability and subsequently yielded higher pure water flux across the membrane [6, 24]. Critically, F3(S2.0) membrane with 2 wt% of PVP and silver NPs loading showed lower contact angle of 66.13 ± 3.44° as compared to F2(S0.5) membrane with 0.5 wt% additives at 68.03 ± 1.31°. The result was in agreement to those reported by Ananth et al. [10] where the increment of silver NPs concentration would enhance membrane wettability. On the other hand, Basri et al. [24] demonstrated that increasing silver NPs from 0.5 wt% to 2.0 wt% could effectively reduce contact angle by 15%. The authors claimed that the presence of silver NPs would lower surface tension of PES, thus allowing water to spread on membrane surface easily. F3(S2.0) membrane exhibited the lowest contact angle value among other sample, This finding is in agreement with Susanto et al. [28] who claimed that membrane with higher porosity on its surface will exhibit more hydrophilicity. In fact, it is testified that more additives tend to contribute to a more porous membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact Angle</th>
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<tr>
<td>F1(S0)</td>
<td>74.73 ± 1.49°</td>
</tr>
<tr>
<td>F2(S0.5)</td>
<td>68.03 ± 1.31°</td>
</tr>
<tr>
<td>F3(S2.0)</td>
<td>66.13 ± 3.44°</td>
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</tbody>
</table>
The improvement in hydrophilicity plays an important role for higher water flux as well as to lower the potential of biofouling as hydrophilic surface generates repulsive hydration force to prevent adsorption of foulant [29]. In addition, the tightly bound water layer that formed on a hydrophilic surface would allow to control the membrane fouling due to foulants could only interact with this water layer.

3.2. Permeability, Porosity and Pore Size All the fabricated membranes were tested with PWP test, while porosity and pore size of membranes were also calculated and displayed in Table 3.

The PWP values of all three membranes fall within the flux range of a nanofiltration (NF) membrane [30]. All the fabricated membranes exhibited high porosity with large membrane pores, which favoured water permeability [7]. In general, addition of inorganic additives [31] and PVP [8] will enhance mass transfer rate between solvent and coagulant during phase inversion. This can result in larger pores formation, increase in membrane porosity and membrane hydrophilicity [32]. For F2(S0.5) membrane, the pore size and porosity decreased slightly with addition of 0.5 wt% silver NPs and PVP. It could be attributed to the silver NPs that had filled up the pores of membrane and successfully well distributed in the membrane matrix, hence producing membrane with lower porosity [10]. Similar findings were reported by Mollahosseini et al. [20] who had incorporated silver NPs into polysulfone to reduce membrane pore size for better pharmaceutical products rejection. In contrary, at higher NPs loading, agglomeration of silver NPs tended to enlarge the membrane pores while leaching of these agglomerated silver NPs during phase inversion would left the membrane with higher porosity [7]. This explained why F3(S2.0) membrane with 2 wt% PVP and silver loading showed the largest membrane pore size accompanied with highest PWP among others.

3.3. Zeta Potential Table 4 tabulates the values of zeta potential of the fabricated membranes. As shown in Table 4, all three membranes show negative zeta potential and this indicates that the membranes possess surface with negative charged at pH 7. Surface charge plays a significant role in foulant rejection in terms of steric repulsion mechanism.

![Table 4. Zeta potential of F1(S0), F2(S0.5) and F3(S2.0) membranes](image)

It was reported that the isoelectric point of HA was pH 3 [22], where beyond that HA would show negatively charge in nature. Thus, the negatively-charged membrane would repel negatively charged HA effectively especially when the feed solution pH was at 8.5.

3.4. SEM and EDX Figure 1 shows SEM cross sectional view, SEM surface view and EDX spectra of F1(S0), F2(S0.5) and F3(S2.0) membranes. From SEM images, all membranes displayed macrovoids with loosely packed structures. This can be attributed to the instantaneous demixing of polymers and solvent at dope solution–water interface during rapid phase inversion. The SEM images and porosity data proved that 15 – 20 wt% of PES in dope would form a porous membrane structure. Besides, finger-like skin and spongy structure sublayer were observed from the SEM cross sectional images and this observation is similar to those reported in Thuyavan and co-workers [1]. F1(S0) and F2(S0.5) membranes showed similar structures with small pore sizes and spongy morphology at sublayer. According to Chong et al. [31], membrane fabricated without the addition of PVP as pore agent would show a short finger-like and spongy structure. This was probably caused by the slow phase inversion rate owing to the hydrophobic nature of PES. From the results, it was found that incorporating 0.5 wt% of silver NPs and PVP into F2(S0.5) membrane did not significantly induce morphological changes. This was in agreement to Ahmad and co-workers [6], who reported a notable difference in membrane morphological changes when inorganic additives exceed 1 wt%. From the SEM images, F3(S2.0) membrane is more porous and possesses uniformly larger pore size as compared to F2(S0.5) membrane. Addition of silver NPs as hydrophilic additives [7] would induce rapid solvent-coagulant exchange and inter-diffusion velocity which eventually accelerate the rate of phase inversion [31]. As a result, longer finger-like structure was observed in F3(S2.0) as compared to F2(S0.5).

The EDX spectra of F1(S0), F2(S0.5) and F3(S2.0) membranes are presented in Figure 1 (g), (h) and (i), respectively. It was clearly shown that no silver NPs trace was found in the pure PES membrane, with only carbon (C), oxygen (O) and sulphur (S) being detected. The initial silver composition in dope solution was 0.5 wt% and 2.0 wt% for F2(S0.5) and F3(S2.0) membranes, respectively.
The detected silver in the EDX analysis was found to be 0.76 wt% and 2.65 wt% for the membranes. One can state that the amount of silver present in the PES/Ag membranes is consistent to the initial silver composition in dope solution for both F2(S0.5) and F3(S2.0).

3.5. Humic Acid Rejection Table 5 shows HA rejections of F1(S0), F2(S0.5) and F3(S2.0) membranes. All three membranes showed high rejection on HA solutes, ranged from 89.55% for F3(S2.0) membrane to 98.64% when using F1(S0) membrane. Other than the repulsion between HA and membrane surface, the pore radius of the membrane also played an important role in rejecting HA. As a long chain organic acid, HA possesses the molecular weight of approximately 5000 Da [33]. In general, NF membranes could reject solutes greater than 1000 Da [34]. Therefore, the fabricated membranes could reject humic acid effectively based on size exclusion mechanism. From the results, the pure PES membrane which possesses the smallest pore radius was found exhibited the highest HA rejection, i.e. 98.64%.

In general, rejection of solutes would be increased in accordance with a decrease in membrane pore size [6]. Besides, smaller membrane pore sizes also prevent HA solutes from entering pore length and thereby reduce the probability of pore blockage. As proven in the SEM images and pore size studies, incorporating PVP and AgNPs would increase membrane pore radius. Rejection of HA reduces with the addition of 0.5 wt% of PVP and silver NPs into F2(S0.5) membrane. At higher PVP and silver NPs loading at 2 wt%, the pore size of F3(S2.0) membrane was 25.25 nm, or approximately 25% larger than those of F1(S0) and F2(S0.5) membranes. Consequently, the rejection of HA was deteriorated significantly to 89.55%.

3.6. Antibacterial Property All membrane samples were exposed to E. coli overnight and SEM was used to observe and examine their bactericidal performance. Figure 2 shows the SEM images of bacteria grown on surface of F1(S0) and F2(S0.5) membranes at 5,000x magnification and F3(S2.0) membrane at 10,000x magnification, respectively. From the SEM images in Figure 2, E. coli were actively grown on the surfaces of F1(S0) and F2(S0.5) membranes. Meanwhile, dead E. coli with irregular-shaped cell wall (marked with circle) were shown on F3(S2.0) membrane. The observable morphology of viable cell magnified at high power microscope would be different with the dead cell [35]. This could be attributed to the fact that the dead cell lost their ability to maintain their rigidity shape, resulting in
the dead cells present with serious shrinkage under high power microscope. However, the viable E. coli bacteria exist in a rod shape and present the highest amount on F1(S0) membrane. This observation was in agreement to the hypothesis made where pure PES membrane does not possesses any antibacterial property. With the incorporation of 0.5 wt% of silver NPs, the amount of E. coli present on F2(S0.5) membrane reduced significantly with severely damaged cell structure. Further increment of silver loading to 2 wt% imparts stronger antibacterial activity, hence the amount of E. coli present on F3(S2.0) membrane is the least among all three membranes. This infers that increasing the amount of silver NPs in membrane would increase membrane antimicrobial activity, similar to those reported in the literature [13].

For instance, Andrade et al. [13] varied the silver loading amount from 0.5 wt% to 2 wt%. It was found that 0.5 wt% was unable to demonstrate a strong antibacterial activity while membrane with 1 wt% and 2 wt% silver NPs loadings both showed 100% inhibition of E. coli. PES/Ag membrane with 1 wt% silver loading exhibited the strongest anti-adhesion performance, thus the authors reported that 1 wt% could be the optimum silver loading in their study. Silver ions are capable of damaging protein structure in bacteria, implying that they are toxic to microorganism, and showing their inhibitory effects toward bacteria [12]. Besides, silver ions also interrupt the electron density and dimerize deoxyribonucleic acid in bacteria [36]. Li et al. [14] pointed out that direct interaction of bacterial cell and silver NPs led to the formation of holes and pits on cellular surface, thus induced the leakage of cytoplasmic material and loss of morphological integrity. In a nutshell, the presence of silver in membrane could impart membrane antimicrobial property while its antibactericidal effect would increase at higher silver loading.

4. CONCLUSION

In this study, silver NPs was impregnated into PES membrane by ex situ blending method.

Three membranes [F1(S0), F2(S0.5) and F3(S2.0)] were fabricated based on different polymer concentrations and additives loadings (PVP and silver NPs). As both PVP and silver loading increased, the pore size and porosity of the membranes increased. This had resulted in higher PWP and lower HA rejection. On top of that, the antibacterial performance of PES/Ag membranes was enhanced significantly at higher silver loading, while the pure PES did not exhibit any antibacterial property. The contact angle results showed that hydrophilicity of membrane increased along with PVP and silver loading, which was deemed to be an advantageous in preventing membrane from biofouling. In brief, the incorporation of silver NPs in PES membranes justified the potential in treating wastewater owing to its enhanced hydrophilicity, permeability, anti-biofouling ability and antibacterial property. F3(S2.0) membrane showed the optimum flux and antibacterial performance among other membrane samples despite of a slight reduction in HA rejection which was tolerable.

5. ACKNOWLEDGMENT

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6. REFERENCES


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