



Research Paper

Modification of Thin Film Composite Nanofiltration Membrane using Silver Nanoparticles: Preparation, Characterization and Antibacterial Performance

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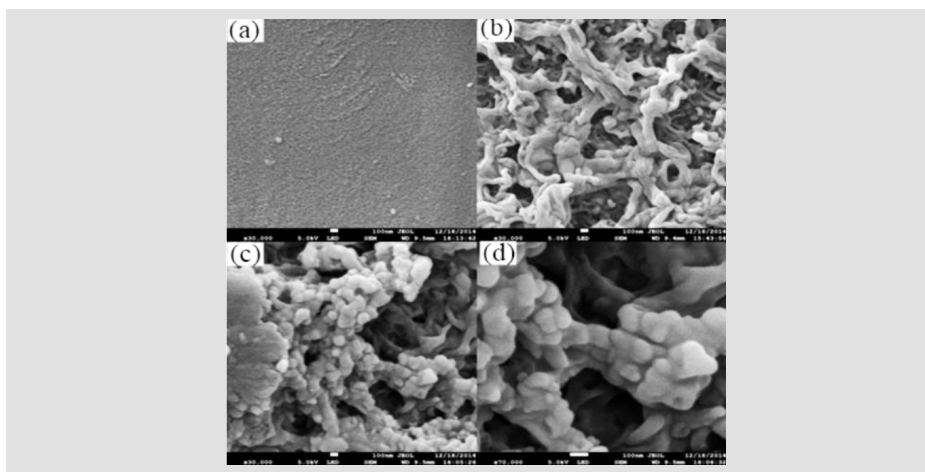
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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Silver nanoparticles as an antibacterial agent to reduce biofouling
- Different aspects of modification of polyamide TFC membranes by silver nanoparticles
- Antibacterial test of low-biofouling modified polyamide TFC membranes

ABSTRACT

This paper reports on preparation of polyamide membrane with addition of silver nanoparticles (AgNPs). AgNPs act as antibacterial agents that are less susceptible to membrane's biofouling by interfacial polymerization (IP) method. AgNPs was synthesized via green route which has been reported previously. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Field emission scanning electron microscopy (FESEM), contact angle measurement, and Energy dispersive X-ray spectrometer (EDX) were carried out to characterize the morphology of the prepared membrane samples. Inhibition zone of *E. Coli* bacteria was used to study the antibacterial behavior of the membranes. As a result, FTIR spectra clearly present the peak of primary amide, secondary amides, carboxyl group and etc. In addition, from the FESEM images, it could be seen that relatively regular and spherical shape AgNPs were formed. Contact angle results revealed that the PA membrane is more hydrophilic than that of the PES membrane. EDX spectra shows a peak that confirmed the presence of AgNPs on PA/Ag membrane. In antibacterial test, the PA membrane alone could not inhibit the growth of *E.Coli*. Membranes with 10 ml and 15 ml loading of AgNPs added to the M-Phenylenediamine (MPD) monomer for the IP process were not enough to kill the *E.Coli* bacteria. The addition of 20ml of AgNPs to MPD monomer however showed an interesting result as we can clearly observe the inhibition zone in the diameter of 1 mm around the circle of the membrane indicate that all bacteria were totally killed.

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1. Introduction

Four types of pressure-driven membrane processes including

microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been commonly used for water/wastewater treatment and

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desalination purposes [1]. Among all, the NF process has been recognized as one of the promising processes for water treatment and portable water production. However, membrane fouling is still become a crucial problem when dealing with membranes which causes flux decline during a certain time operation.

Membrane fouling occurs when there is a blockage in the membrane pores during filtration by adsorption of particulates and compounds onto the membrane surface or within the membrane pores. Pore blocking slows down the permeate production rate and increases the difficulty of the membrane filtration operation. In general, there are four types of fouling, including organic fouling, crystalline/scaling fouling, particle/colloid fouling and biofouling [2]. Various attempts have been done to reduce fouling effect. For instance, pre-treatment of the feed stream [3], modification of the membrane surface features (e.g. hydrophobic or hydrophilic surface, and electronegative or electropositive charge) [4] and periodic cleaning [5]. For example, small attachment of microorganism (i.e. bacteria and viruses), excrete extracellular polymeric substances (EPS) on the membrane surface could cause biofilms formation. Thus, this can enhance biofouling to occur later on [6].

In the past, chlorination had been one of the ways for controlling the microbes. Besides that, an alternative approach to reduce microbial biofouling is by modifying the membrane surface. Through this method, it is believed that the modified surface not only has an ability to inhibit the bacteria growth, but also to kill the bacteria. Based on previous research findings, it was observed that for biofouling properties, the TiO₂ self-assembled TFC (thin film composite) membrane could only work effectively by assistant of UV illumination where additional energy required for the UV light system; thus, it contributes to high operational cost [7]. Inorganic materials like silver (Ag) are suitable to be an antimicrobial agent to kill bacteria or inhibit its growth since it is effective against a broad spectrum of both gram-negative and gram-positive bacteria and fungi [8, 9].

A few methods are available for the synthesization of AgNPs such as chemical reduction [10], photochemical reduction [11], microwave [12] and recently via the green chemistry method [13]. Previously, the synthesis of the silver and palladium nanoparticles at room temperature also had been done by using the coffee and the tea extracts [14].

In this paper, antibacterial polyamide NF membranes were prepared by adding AgNPs into the MPD monomer during the IP process. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Field emission scanning electron microscopy (FESEM), contact angle measurement, and Energy dispersive X-ray spectrometer (EDX) were carried out to characterize the morphology of the prepared membranes while inhibition zone of *E. Coli* bacteria was used to study the antibacterial behavior of the membranes.

2. Experimental

2.1. Materials

Silver nitrate was purchased from Sigma Aldrich. Nutrient broth and Mueller Hinton agar powder, a product of Oxoid which all were supplied by Thermo Scientific. Dry tea leaves were bought from Malaysia tea plantations. All glassware have washed with distilled water and have dried in the oven before use. The strain employed throughout this study *Escherichia Coli* (0157:H7) (ATCC 43888) was obtained from Central Laboratory of Universiti Malaysia Pahang (UMP). It was cultured on nutrient agar slants and kept at 4° C. The commercial PES ultrafiltration (UF) flat-sheet membrane as a substrate for preparation of polyamide NF membrane was supplied by Amfor Inc (China). The characteristics of the PES UF support membrane were listed in Table 1. Both M-Phenylenediamine (MPD) and Trimesoyl Chloride (TMC) were supplied by Acros.

Table 1. Characteristics of UF PES Membrane.

Membrane	UF PES50
Material	Polyethersulfone
Nominal MWCO	50,000 Da
Water Flux @ 25°C	260 LMH

2.2. Preparation of membranes via IP method

The procedure for fabricate the membrane samples is according to a past research with some modifications [15]. Firstly, the PES UF membrane was immersed in DI water overnight, then removed from water and placed on an acrylic plate. A gasket and an acrylic frame were put on the top of the support

membrane and were attached by using the binder clips. At the same time, both 2% (w/v) MPD solution and 2% (w/v) MPD/AgNPs solution were prepared. The 2% (w/v) MPD/AgNPs solution was prepared by mixing different volumes of AgNPs solution (i.e. 10ml, 15ml, 20ml, 25ml, 30ml and 40ml) with the MPD. Afterwards, the MPD aqueous solution was poured onto the frame and allowed to contact with the UF support for about 30 minutes in order to let the solution to penetrate into the pores of the PES UF support layer. The frame was let to stand vertically at ambience temperature in order to drain the excess solution. After that, the TMC in the organic solution (i.e. hexane) was poured into the frame. After certain times (e.g. 10s, 30s and 60s), hexane was drained from the frame, and the frame and gasket were disassembled. The new PA membrane was washed by hexane and left to dry in the oven at 60°C for 15 minutes. Finally, the prepared membrane was stored in DI water prior to study its characterizations. The same steps were repeated for 2% MPD/AgNPs aqueous solution.

2.3. Membranes structure and surface characterization

Chemical characterization of the membrane surface was accomplished by ATR-FTIR spectroscopy instrument with Thermo Nicolet Avatar 370 Fourier transform infrared spectrometer. Membrane surface and cross-section morphology were characterized by the FESEM. The presence of silver on the membrane surface was evaluated by using Oxford X-Max EDX coupled with the FESEM. For the membrane hydrophilicity, the contact angle was measured using the sessile drop method with a contact angle goniometer.

2.4. Membrane pure water permeability (PWP)

Each freshly prepared membrane was first flushed with deionized water in an Amicon stirred cell (model 8200) using 4 bar pressure for at least 10 minutes at ambient temperature. Following that, water flux was measured under different pressures, e.g. 1, 2, 3 and 4 bar with deionized water at ambient temperature. About 10 ml of permeate was collected and the total time taken was also recorded to calculate the water flux, J by the following equation:

$$J = \frac{V}{A\Delta t} \quad (1)$$

whereby A is the effective surface area of the membrane sample (28.7 cm²) and V is the volume of the permeate collected (10 ml). By plotting a graph of the flux versus the operating pressure, the membrane permeability Pm can be obtained from the slope of the straight line as follows:

$$Pm = \frac{J}{\Delta P} \quad (2)$$

2.5. Actimicrobial assays of low-biofouling PA/Ag membranes

The antibacterial activities of membrane samples which contained various volumes of the AgNPs were studied against the *E. Coli* bacteria. The procedure from Basri et al. [16] was used in experiments. Firstly, antibacterial activity of the prepared membranes was investigated by the agar diffusion method against the *E. Coli*. Kirby Bauer technique was applied in the preparation of media-culture plate containing the *E. Coli*. The membranes were cut into circular-disks, autoclaved and then put on the bacteria media-culture at 37 °C incubation temperature overnight. The antibacterial activity of the membrane was determined by inhibition ring that formed after 24 h incubation. The growth inhibition was visually detected on the next day after incubation. All tests were repeated twice.

3. Results and Discussion

3.1. Visual Observations of the membrane samples

The procedure for fabricating membrane samples is the interfacial polymerization (IP) technique between the MPD and the TMC with different loading concentration of the AgNPs. Figure 1 shows the appearances before and after modification of membranes.

From Figure 1, significant differences in color between each membrane sample were observed. The PES UF membrane initially in white color changed to brown color (b) after being modified with the MPD-TMC. This happened due to the contribution of dark brown color of the MPD solution itself. The addition of AgNPs did not give much influence to the surface color of the membrane samples. Overall, (c) gave the best result in the

antimicrobial assay which could inhibit the bacteria at a very minimum loading of the AgNPs.

3.2. ATR-FTIR

The chemical compositions of the surface of the PA nanofiltration membranes were investigated by ATR-FTIR instrument. As a comparison, the FTIR spectra of the PES supporting membrane and the reactive monomers (MPD and TMC) were also displayed as references. The obtained results were demonstrated in Figure 2. The IP reaction between the aqueous MPD solution and the organic TMC solution is known to produce PA. Two types of reactions are expected when considering dysfunctional amine in the MPD and trifunctional chloride in the TMC. First one is the network crosslinking reaction of the amine in MPD with the third remaining chloride group in the TMC via amide linkage. The other is the hydrolysis of the third chloride to carboxylic acid, providing hydrophilicity in the membranes [17].

From the spectra above, the primary amide (i.e. NH_2 stretching at 3362.94 cm^{-1} and 3366.45 cm^{-1}) is obviously presented. The amide (II) band for secondary amides is due to the coupling of N-H bending and C-N stretching and appears at 1547.69 cm^{-1} and 1546.89 cm^{-1} . The presence of a carboxylic group (i.e. C=O at 1610.05 cm^{-1} and 1610.94 cm^{-1}) indicates the hydrolysis of third chloride to carboxylic acid, providing hydrophilicity to the membranes. Table 2 summarized the infrared bands of the membranes.

3.3. FESEM

Figure 3 shows the unmodified PES UF membrane and the PA membrane

with and without addition of the AgNPs, respectively. The FESEM pictures were taken under 30,000x magnifications (a, b and c) and 70,000x magnification (d). From the figure, it can be observed that the IP reaction generates another layer on the top of the PES supporting membrane (b) and as for the membrane modified with the mixture of MPD and AgNPs (c and d), the existence of the AgNPs can be observed obviously on the top surface of the membrane.

Basri et al. reported that cubic and spheres shape of the AgNPs was observed eventhough at low Ag-loading (PES-Ag0.5P360) [18]. From the same figure, it could be observed that relatively regular and spherical shape AgNPs were formed. The membrane loaded with the AgNPs (c) showed rougher surface morphology compared to membranes without the AgNPs (a, b). The particles in the membrane (c) were identified to be approximately spherical in shape. This result is in good agreement with the finding reported previously in which the AgNPs observed on the membrane surface showed spherical shape, too [19]. Nevertheless, from the lower magnification of the PA/Ag membrane which is 10,000x magnification (Figure 4), agglomeration of the AgNPs was occurred and this may be happened due to the existence of the capping ligand from the tea extract.

Table 2. Characteristic infrared bands of PA membranes.

Wavenumber (cm^{-1})	Assignment
3362.94 cm^{-1} and 3366.45 cm^{-1}	primary amide, NH_2 stretching
1547.69 cm^{-1} and 1546.89 cm^{-1}	secondary amide N-H bending, C-N stretching
1610.05 cm^{-1} and 1610.94 cm^{-1}	carboxylic group, C=O

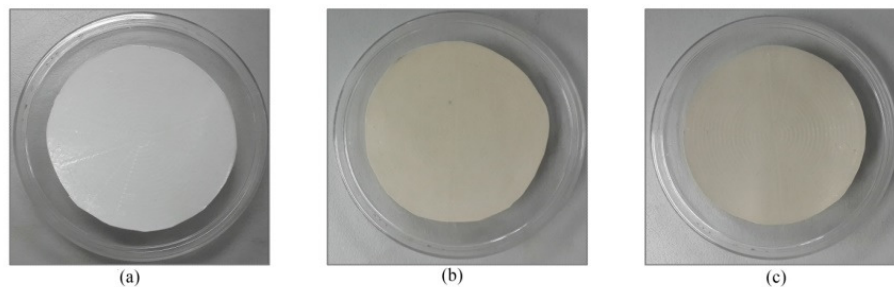


Fig. 1. Membranes (a) unmodified UF PES membrane (b) NF PA membrane and (c) NF PA-Ag membrane.

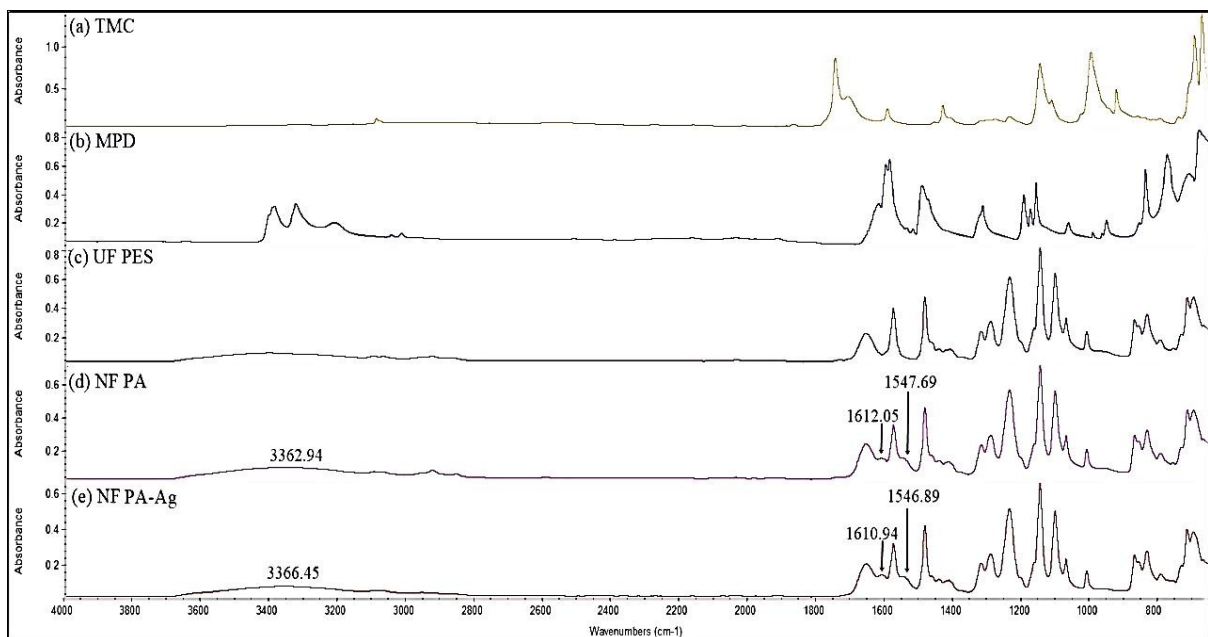


Fig. 2. FTIR spectra of (a) TMC; (b) MPD; (c) UF PES membrane; (d) NF PA membrane and (e) NF PA/Ag membrane.

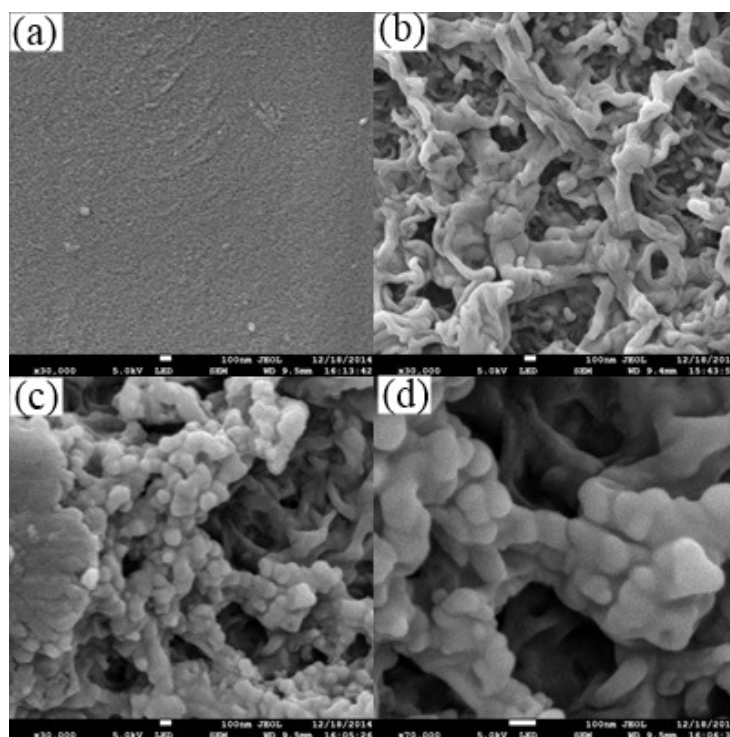


Fig. 3. Surface FESEM micrographs of (a) unmodified PES membrane, (b) PA membrane, (c) PA/Ag membrane and (d) PA/Ag membrane (with higher magnification).

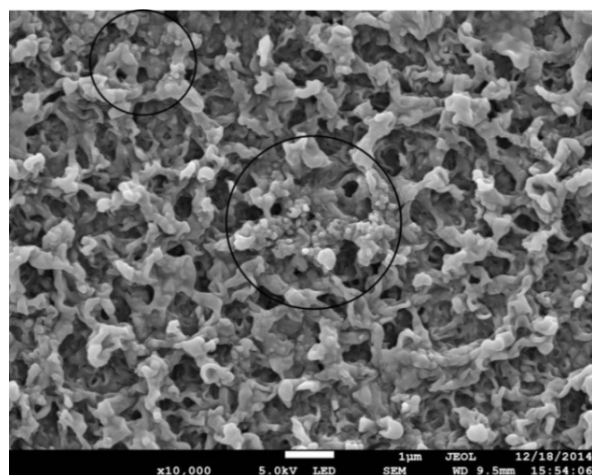


Fig. 4. Surface FESEM micrograph of PA/Ag membrane at 10,000x magnification.

3.4. EDX

Presence of the AgNPs on the PA/Ag membrane surface is confirmed by the EDX spectra. Figure 5 a-c showed the FESEM images and EDX spectra of selected areas that have pictured from different membranes with 20 ml, 30 ml and 40 ml silver loading.

From the EDX spectra, one can see the peaks that confirmed the presence of the AgNPs on PA/Ag membranes. Compositions of different elements are reported in Table 3. Previous reports was also confirmed the presence of the AgNPs by using similar approach [20,21].

3.5. Membrane hydrophilicity determination

The static method of the sessile drop technique was performed to measure the water contact angle (i.e. hydrophilicity or hydrophobicity) of the unmodified and modified membrane samples [22]. In sessile-drop method, contact angle values are measured over more than five times of different spots to ensure the measurement precision. Each final contact angle values were obtained by averaging all of the values taken. Figure 6 shows the contact

angle of the PES membrane and the six PA membranes with different reaction time. Based on the figure, it can be observed that the contact angle values for modified membranes were lower than that of unmodified membrane (the control sample). It can be concluded that the six PA membranes become more hydrophilic after modification. The percentage decrement of the modified membranes was in the range of 6.4% to 24.2%. This phenomenon could be attributed to the presence of the Ag particles that has lowered the surface tension of pristine PES. The decrease of contact angle of the PA membranes were in agreement with the reports in literature [23, 24].

Table 3. Elements compositions (percentage) of PA/Ag Membranes.

Membranes	C	O	N	S	Ag
PA/Ag20	57.1	20.5	13.2	8.6	0.7
PA/Ag30	56.4	21.2	12.0	8.8	1.6
PA/Ag40	54.8	19.7	11.5	11.4	2.6

3.6. Membrane PWP

Pure water flux (J_w) was measured for the membrane support (UF-PES membrane) and the polyamide membrane at different operating pressures, ΔP , as shown in Figure 7. Pure water permeability, P_m , was determined from the gradient of the straight line in Figure 7. It is worth noting that both polyamide membranes (PA and PA/Ag) exhibited lower permeability than that of the support UF-PES membrane. The measured permeability values were in the range of values reported previously for NF membranes [23]. The lower permeability for the modified membrane is attributed to the formed denser layer or thicker layer of polyamide formed on the membrane surface increase the membrane resistance. From the result obtained, it was found that adding some nanoparticles slightly change the membrane permeability but it was not too significant.

3.7. Antimicrobial assays of low-biofouling PA/Ag membranes

Based on a previous research by Lee et al. [23] which prepared PA/TiO₂ nanocomposite membranes using the MPD and the TMC solutions containing 10 wt% of the AgNPs by *in situ* IP reaction. Membranes were tested against *P. aeruginosa* bacteria and successfully reduced the biofouling effect. Despite that most of the AgNPs remained on the membrane surface, some nanoparticles were also trapped in the bulk of the active layer reducing the

antifouling activities [23].

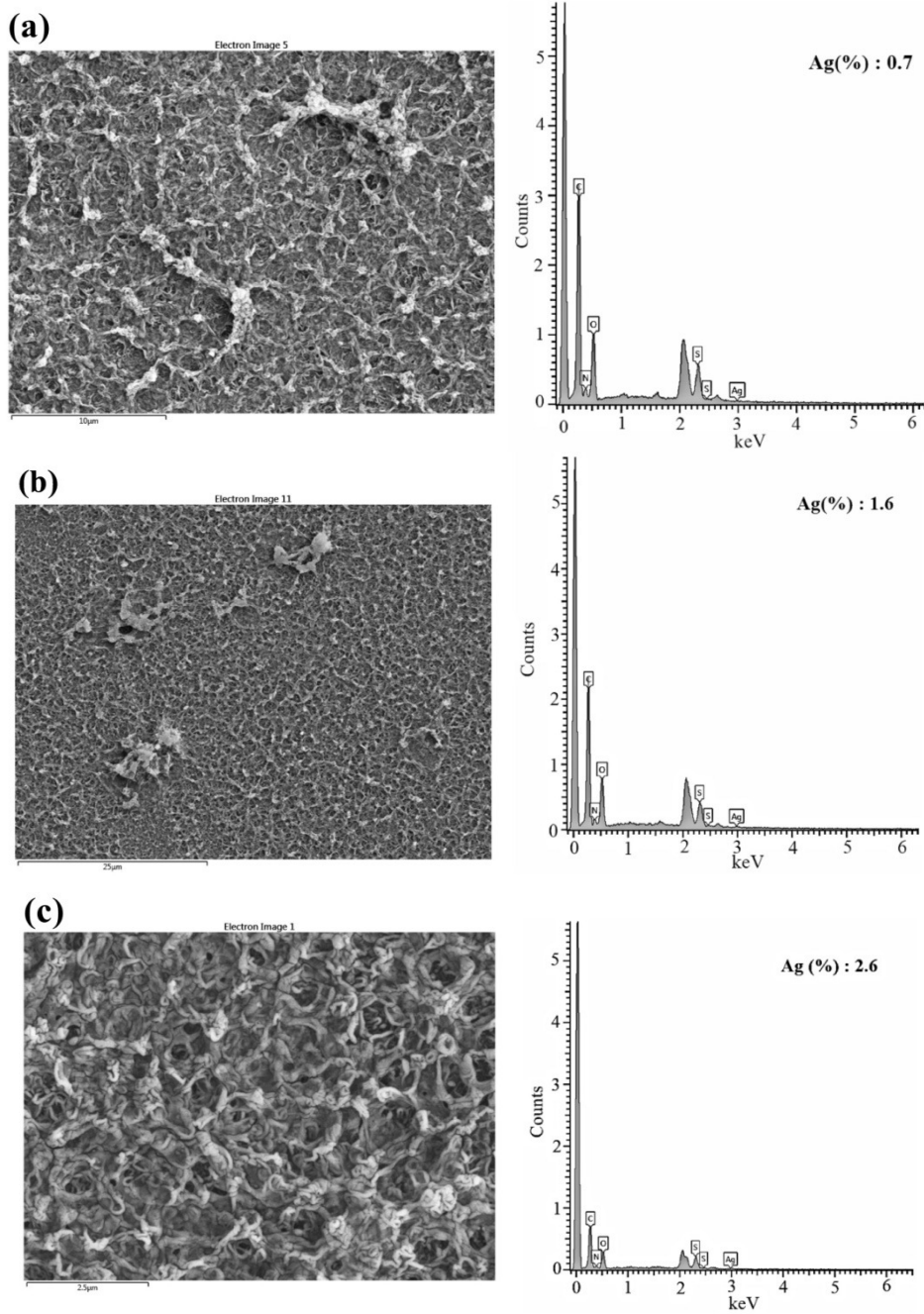
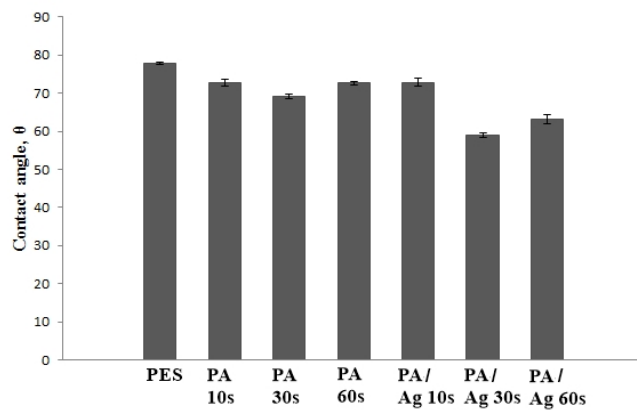


Fig. 5. FESEM images and EDX spectra of PA/Ag membranes (a) PA/Ag20 membranes (b) PA/Ag30 membranes (c) PA/Ag40 membranes.



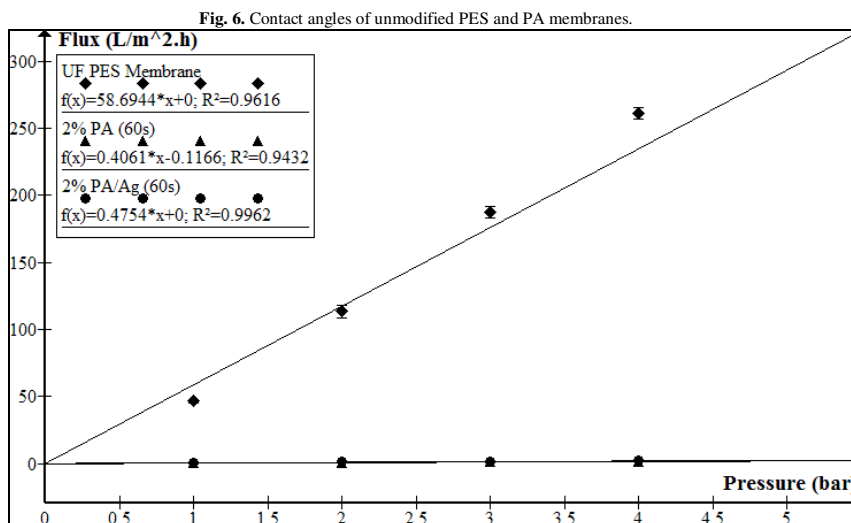


Fig. 7. Permeate flux versus transmembrane pressure of different membranes.

Disc diffusion method was used for susceptibility testing of the *E. Coli* bacteria. Literally, the antibacterial capability of the PA/Ag membranes could be observed from the inhibition zone area [24, 25]. Figure 8 shows the inhibition areas of bacterial growth against the *E.Coli* for the modified membranes with or without addition of the AgNPs. M0 is a PA membrane sample without the AgNPs, used as control membrane whereas M1, M2 and M3 are PA/Ag membranes with addition of 10 ml, 15 ml and 20 ml of the AgNPs, respectively. The areas around the silver-pregnant membrane should be brighter as the bacteria could not grow up there due to the bacteriostatic effect of the membrane itself [20].

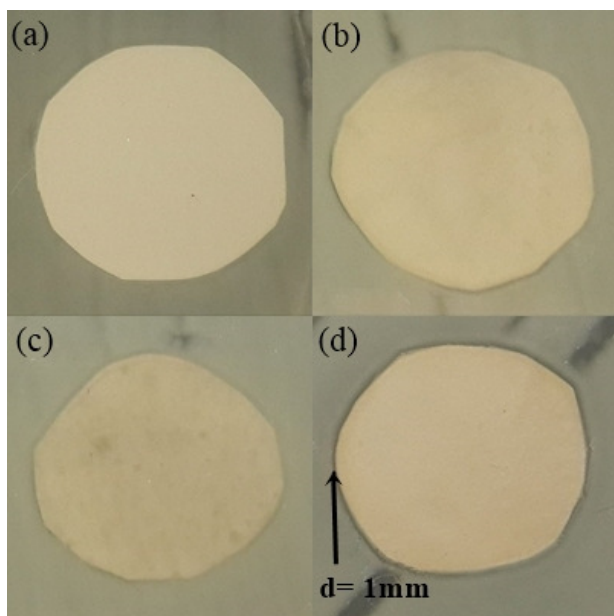


Fig. 8. Antimicrobial activities of (a) M0, (b) M1, (c) M2 and (d) M3 membranes against *E. Coli*.

From the picture, it obviously observes that the PA membrane alone (M0) could not inhibit the growth of the *E.Coli*. In addition to that, membranes with 10 ml (M1) and 15 ml (M2) of the AgNPs were not enough to kill the bacteria as bacteria colonies are still available around the membrane circle. However, the addition of 20 ml of the AgNPs showed an interesting result as we can clearly see the brighter zone that indicates the inhibition zone in the diameter of 1 mm around the circle of M3 membrane. The current finding seemed to be similar with other research findings in the literature [21]. Based on this result, M3 selected as the low-biofouling TFC membrane to be used in the next membrane separation experiments. The description of monomers and silver compositions that had been used to

produce the membranes was listed in the Table 4.

Table 4. Monomers and AgNPs compositions of membranes.

Membrane	MPD (wt%)	Silver Loading (ml)	TMC (wt%)
M0	2	0	0.15
M1	2	10	0.15
M2	2	15	0.15
M3	2	20	0.15

4. Conclusions

This study demonstrates a preparation of various polyamide membranes via the IP method. A series of experimental results confirmed that the certain amount of the AgNPs loading into the MPD monomer was successfully produced the PA-Ag membrane. The FESEM results revealed that the IP reaction had generated a new layer on the top surface of the PES-UF membrane support and after some modifications; one can clearly see the existence of the AgNPs. The membrane loaded with the AgNPs showed rougher surface morphology compared to membranes without the AgNPs. However, some agglomeration of the particles was detected due to the existence of the capping ligand. From the antimicrobial test result, the PA/Ag membrane loading with 20 ml of the AgNPs (0.7 wt% AgNPs deduced by EDX) was capable to inhibit bacteria growth against the *E.Coli* bacteria. Thus, this membrane was selected as the low-biofouling NF membrane and will be used in the next membranes performance experiment in future.

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