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Development of Polyethersulfone (PES)/Silver Nanoparticles (AgNPs)/Polyethylene Glycol (PEG) Nanofiltration Membrane

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Abstract. Nanofiltration is a membrane-based separation process that has been used widely in the separation and purification fields for various applications such as dye desalting, applications of water softening, pharmaceuticals and wastewater treatment. In this research, polyethersulfone (PES), polyethylene glycol (PEG), Pluronic F108 and silver nanoparticles (AgNPs) nanofiltration membrane was prepared using casting solution technique with N-methyl-2-pyrrolidone (NMP) was used as a solvent. The effects of Pluronic F108 and silver nanoparticles (AgNPs) concentrations in the casting solutions on the membrane performance/properties were also studied. The membrane pure water permeation (PWP) and salt rejection tests were carried out for membrane performance analysis. Scanning electron microscopy (SEM) was used for the membrane morphology characterization. Fourier transform infrared spectroscopy was utilized to identify functional groups in the membrane. Membrane with 2.0 wt.% of Pluronic F108 and 0.05 wt.% of AgNPs showed the best performances for both PWP (40.89 L/m^{2}h) as well as permeation flux of salts solution of NaCl (43.95 L/m^{2}h), Na_2SO_4 (21.16 L/m^{2}h), $MgCl_2$ (26.46 L/m^{2}h) and $MgSO_4$ (20.41 L/m^{2}h). All fabricated membranes with different formulation of dope composition obtained high salts rejection in the range of 79% to 91%. SEM images showed addition of AgNPs has improved fabricated membrane morphology with higher pore density and larger macro-void structure.

INTRODUCTION

Membrane separation is a promising and emerging technology that offers great potential for various types of industrial applications. Due to the versatility and efficiency of nanofiltration (NF) membrane, this type of filtration membrane is an attractive alternative for specialized industrial applications especially for water and wastewater treatment. In this research study, the fabricated membranes were tested for removal of salts consisting of divalent salts which are sodium sulphate (Na_2SO_4), magnesium chloride ($MgCl_2$) and magnesium sulphate ($MgSO_4$) and monovalent salt of sodium chloride (NaCl). Polyethersulfone (PES) is one the most suitable polymer for fabrication of membrane as it has high mechanical property, good heat resistance and environmental endurance [1]. However, it has some disadvantages as it is highly hydrophobic, which can lead to low antifouling properties. To prevent fouling, it requires improvement and modification to enhance its hydrophilicity and antifouling properties [2].

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Many modifications had been recorded for these past few decades, which divided into physical methods and chemical methods. Physical methods involve blending and surface coating method, whereas chemical methods consist of photo-induced grafting, gamma ray and electron beam-induced grafting, plasma treatment and plasma-induced grafting, thermal-induced grafting and immobilization, surface-initiated atom transfer radical polymerization [3].

Generally, in this study, blending of additives polyethylene glycol (PEG), non-ionic surfactant (Pluronic F108) and silver nanoparticles (AgNPs) with PES was performed in order to increase membrane hydrophilicity and anti-fouling properties. AgNPs have been reported to have antibacterial activities and cytotoxicity. Addition of AgNPs in membrane matrix via blending method can prevent formation of biofouling and its effectiveness depends on the location of AgNPs in membrane matrix, as the location of AgNPs can change the diffusivity or release of ionic silver (Ag^{+}) [4]. Therefore, in this study, the effectiveness of addition of different amount of AgNPs in the fabricated membranes was evaluated through measurement of pure water permeation (PWP), salt rejection performance and morphological evaluation by SEM analysis.

MATERIALS AND METHOD

Dope Formulation and Preparation

The membranes were prepared by phase inversion technique consisting prescribed amounts of dope formulation of PES, PEG 600, N-methyl-2-pyrrolidone (NMP), Pluronic F108 non-ionic surfactant and AgNPs. For the first membrane formulation (M1), there was no addition of AgNPs and this membrane was used as a control. The other membrane formulations as tabulated in Table 1 having varying amount of NMP and AgNPs, while the amount of PES and PEG were kept constant. The prepared dope solutions were stirred for 8 hours in order to obtain homogenous solutions. The process continued with immersion in a water bath for 24 hours and then ethanol for another 24 hours. The resulted membranes were again soaked in n-hexane for 3 hours to improve membrane separation properties. Lastly, the prepared membranes were allowed to dry at room temperature to eliminate air bubble.

TABLE 1. Dope formulation

Dopes	PES (wt.%)	NMP (wt.%)	PEG (wt.%)	F108 (wt.%)	AgNPs (wt.%)	H_2O (wt.%)
M1	21	72.3	2	1	-	3.7
M2	21	71.25	2	2	0.05	3.7
M3	21	70.20	2	3	0.10	3.7
M4	21	68.80	2	4	0.50	3.7

Membrane Casting

The membranes were fabricated by using dry/wet phase inversion via the immersion precipitation technique. The newly formulated dope solutions were cast onto a glass plate as a support layer with casting knife setting at 150 μm. Then, the glass plate, together with the membrane, were immersed in a water bath for 24 hours until coagulation completed. The immersed membranes were soaked in ethanol for another 24 hours followed by n-hexane immersion for about 2-3 hours before dried at room temperature for at least 24 hours.

Membrane Permeation Performance

Pure Water Permeation

The pure water permeability or the water flux of NF membranes were conducted using a dead-end filtration cell. First, the membrane was cut into appropriate size to fit with the cell filtration. Then, the cell filtration was filled with 100 ml distilled water and the membranes were compacted for 30 minutes at 5 bar. The permeation flux was measured using the following equation:

$$\text{Permeation flux, } J_W = Q/\ (A.\Delta T)$$

Where,

J_W = the permeate flux (L/m^2h)
Q = volume of permeate solution collected (L)
A = area of membrane (m^2)
ΔT = permeation time of membrane (h)

Salt Rejection Test

Monovalent (NaCI) and multivalent salt solutions ($MgSO_4$, $MgCI_2$, and Na_2SO_4) were used as a feed solution. The conductivity meter was used to measure salt concentration in the feed, permeate and retentate of each rejection test of the fabricated membranes. The following equation was used to calculate the percentage of salt rejection:

$$\text{Retention of rejection, R (\%)} = (1-C_p/C_f) \times 100$$

Where,

R = retention of rejection (%)
C_P = ion concentration of solute permeation (mg/L)
C_f = ion concentration of solute feed (mg/L)

Membrane Characterization

The fabricated membranes were tested by using Fourier transform infrared (FTIR) spectrophotometer to analyze the functional groups that exists in the membranes. Scanning electron microscopy (SEM) was used to analyze the surface and cross-section morphology of the fabricated membranes.

RESULTS AND DISCUSSION

Pure Water Permeation Test

In this research, the measurement of water flux as a function of applied pressure was implemented to evaluate the stability and hydraulic properties of NF membrane. After about 15-20 minutes of compaction process, the pure water permeability for each membrane sample was verified at five different pressures (3 bar, 3.5 bar, 4 bar, 4.5 bar, and 5 bar). Permeate was then collected at a steady state condition. The NF membranes permeability were calculated and illustrated in Fig. 1.

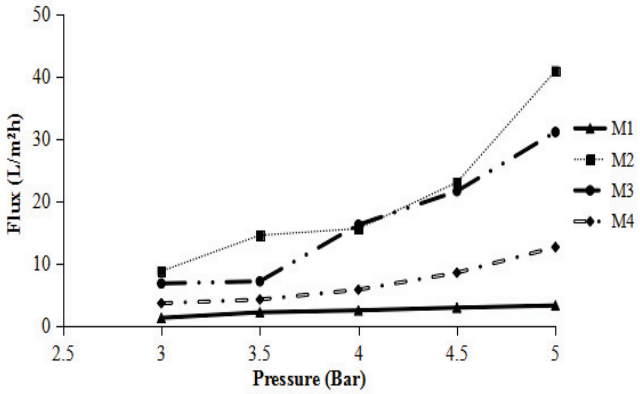

FIGURE 1. Pure water permeation (PWP) of NF membranes

Results obtained in Fig. 1 shows strong connection of hydrophilicity with the membrane performances. In this study, membrane 2 (M2) shows the highest flux for PWP of 40.89 L/m^{2}h at 5 bar while membrane 1 (M1) has the lowest flux with 3.22 L/m^{2}h at the same pressure indicating 38% improvement in the permeability of membrane. Figure 1 also indicates in general PWP of all membranes with addition of AgNPs has increased in comparison to M1 with the highest was obtained by M2. The relatively high PWP of M2, M3 and M4 might be contributed by the addition of Pluronic F108 and AgNPs which improved the porosity of the membrane surface [5, 6]. Low PWP value was observed with M4 and this might be due to the decrease of pore size and pore density or agglomeration of added surfactant and AgNPs in the developed dope solutions [7]. Furthermore, previous study has reported addition of more than 2% and 0.05% of Pluronic F108 and AgNPs, respectively can increase the viscosity of the casting solution [8], which later resulted in the decrease of membrane pore size and porosity.

Flux and Salt Rejection Test

Salt permeate flux and salt rejection tests were performed with 0.01 M of NaCl as monovalent salt and 0.01 M of Na_2SO_4, $MgCl_2$ and $MgSO_4$ as divalent salts under 5 bar operating pressure using dead-end filtration cell with an effective membrane area of 0.00139 m^2. The salt permeate flux of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ for M1, M2, M3 and M4 are shown in Fig. 2. Generally, M2 displays the highest flux for four different salts solutions in comparison to the other membranes. Similar to the trend observed in Fig. 1, high permeability was observed with M2 in Fig. 2 that can be contributed to the ideal amount of Pluronic F108 and AgNPs added in the dope solution. Excess in Pluronic F108 can cause decrease in pore size thus decreasing membrane porosity while excess in nanoparticles can cause clumping between particles which lead to membrane blockage [9].

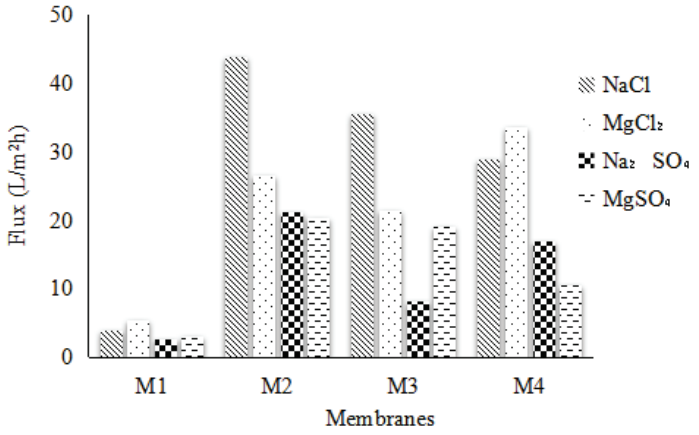

FIGURE 2. Permeation of NF membranes for NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$

Figure 3 shows separation performance of different membrane formulation with rejection capacities of NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$ salt solutions. Overall, the salt rejection trends can be simplified in the order of Na_2SO_4 > $MgSO_4$ > $MgCl_2$ > NaCl. This might be due to the negatively charged PES membrane surface which contributed to the high rejection for multivalent SO_4^{2-} anion (>90%), and is a typical characteristic of most nanofiltration membrane. The presence of bivalent cation (Mg^{2+}) causes slight decrease in the rejection of sulfate anion. This is because the rejection performance of NF membrane towards charged solute is controlled by both the steric size exclusion and Donnan exclusion effects. Therefore, the negative charges on the membrane surface rejected the higher valence sulfate anion more than the monovalent chloride anion [8]. The observed salts rejection as shown in Fig. 3 were in the range of 80% to 91%. Similar to the trend obtained with the previous PWP test, M2 shows the highest rejection for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ salts solutions in comparison to the other membrane formulations. These proved that M2 displayed the best rejection with optimum amount of Pluronic F108 and AgNPs in the membrane formulation. Addition of Pluronic F108 in membrane dope solution causes increase in membrane hydrophilicity with excellent fouling resistant characteristic. Pluronic F108 consists of long polyethylene oxide

(PEO) chains that provide high repulsion forces, together with desolvation effects which make membranes to have high fouling-resistant ability [9].

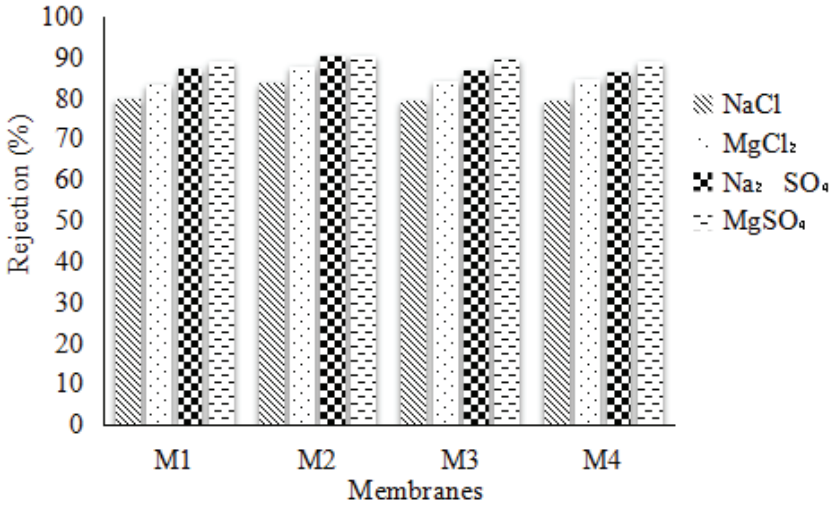

FIGURE 3. NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$ rejection of four NF membranes at 5 bar

Characterization of Nanofiltration Membrane

Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to detect the presence of functional groups in the fabricated NF membranes. The wavelength range is 4000-600 cm^{-1} and the spectra were obtained from a 200 µm diameter sampling area. Figure 4 shows the obtained FTIR spectra, where all membrane types exhibited almost similar peak due to the same chemical composition content in the prepared dope solutions, except for M1 which lacked AgNPs. Figure 4 displays the following functional group of C=O, C-O, C-H and O-H. These are the main peaks exhibited by PES, PEG, Pluronic F108 and AgNPs nanofiltration membranes. The membrane exhibited peaks at 1154 cm^{-1} suggesting symmetric stretching vibration of sulfone group S=O. The wavenumber at 1241 cm^{-1} proved the presence of C-O group. The peaks presence in the range of 2957 cm^{-1} to 2916 cm^{-1} and 2899 cm^{-1} to 2876 cm^{-1} indicated the presence of CH_3 asymmetric aliphatic stretching and symmetric aliphatic stretching, respectively. The C_6H_6 ring stretch has wavenumber of 1581 cm^{-1} which is not shifted due to strong bonding or stable condition of aromatic ring. Next functional group is the C-H group in phenyl ring substitution band which at 853 cm^{-1}. Lastly, O-H stretched was recorded in all four membranes at bands from 3482 cm^{-1} to 3432 cm^{-1}. This O-H may indicate the presence of ethanol during post-treatments of the membranes.

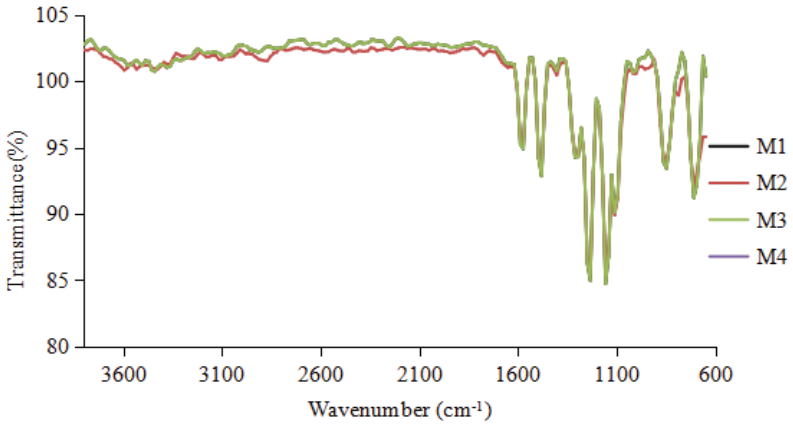

FIGURE 4. FTIR spectra of NF fabricated membranes

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images of cross sectional morphology of the fabricated NF membranes of M1 and M2 are presented in Fig. 5 and 6 at two magnifications (750x and 2000x). M1 (control membrane) and M2 (membrane with the best PWP, flux and salts rejection tests) were selected for comparative assessment on the effects of AgNPs towards membrane morphology and porosity. Both M1 and M2 displayed a porous and finger-like structure with dense top layer. These characteristics are typical features of asymmetric membranes as reported by Hosseini et al. [10]. It was also reported that the skin layer of membranes plays important role in controlling flux and rejection performance due to its relatively thin and compact form while porous sublayer was providing mechanical strength. Surface morphologies of membranes are greatly affected by the kinetic and thermodynamic of system during the phase inversion process [7]. The addition of ideal concentration of nanoparticles in polymeric solution can result to formation of a more uniform casting solution, which could lead to the increase in solvent and non-solvent exchange rate, thus creating larger pore channels [8, 10]. As depicted in Fig. 5 and 6, M2 has higher pore density and larger macro-void sublayer structure in comparison to M1. As mentioned, the reason can be due to kinetic and thermodynamic effects. Differences in morphological characteristics between these two membranes might be due to the rapid exchange of solvent and non-solvent in the phase inversion process with increasing hydrophilicity in M2 casting solution which was induced by the hydrophilic AgNPs [11]. Observations obtained through SEM images were consistent with the earlier tests conducted on PWP, flux and salts rejection tests, which showed better performances of M2 in comparison to the other fabricated membranes, particularly M1.

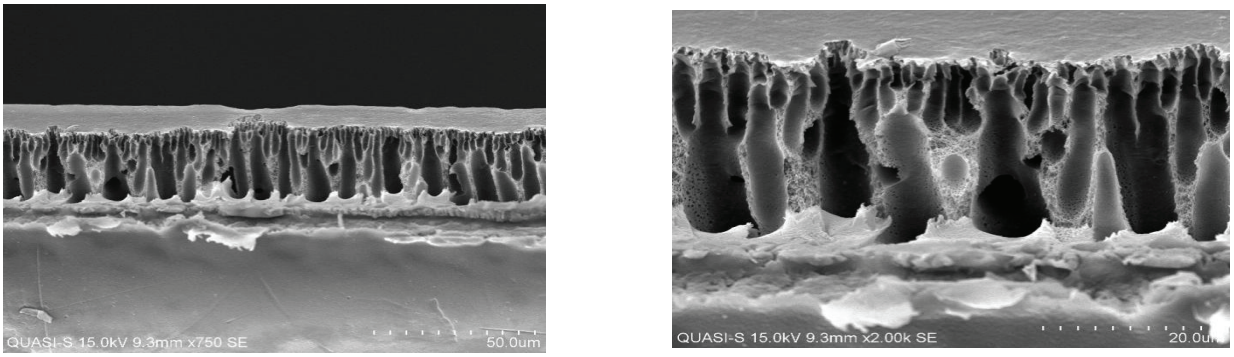

Figure 5. Cross-sectional SEM images of M1

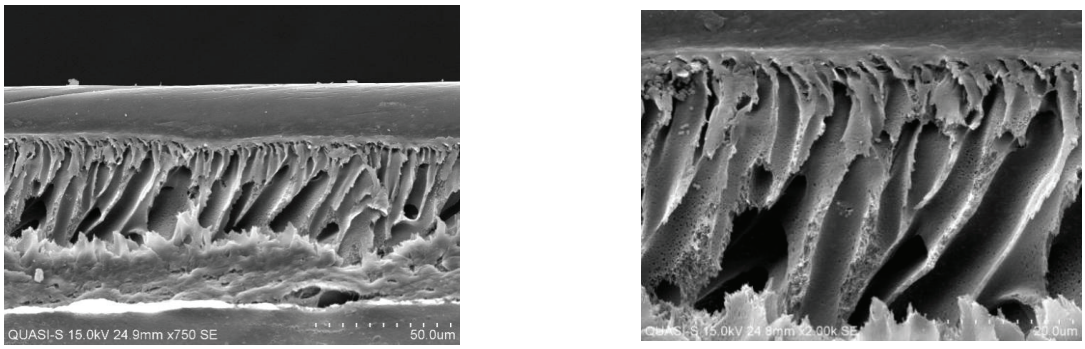

Figure 6. Cross-sectional SEM images of M2

Figure 7 shows the surface of M1 and M2, with the later having smoother morphology and higher pore density. This also indicates fine dispersion of AgNPs outside and inside the PES matrix and no obvious occurrence of agglomeration of the added nanoparticles. Furthermore, no cracks were detected on the membrane surface of M2, signifying that the membranes was not brittle and the addition of AgNPs had no detrimental effect on the membrane stability.

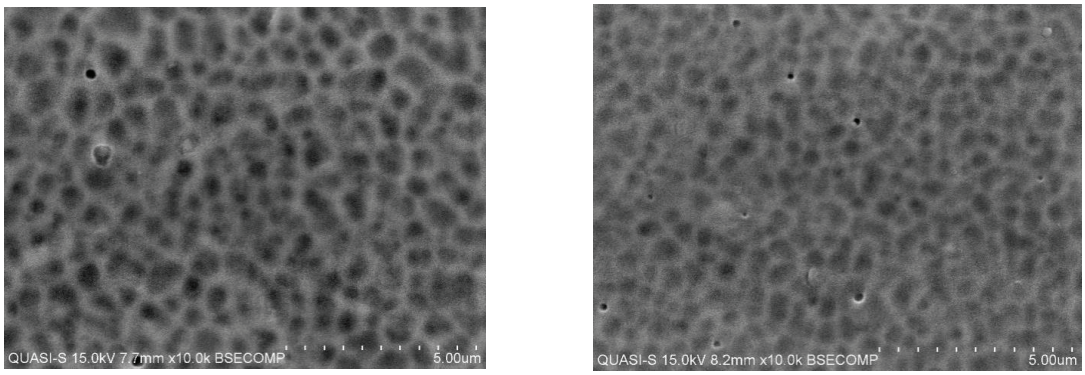

Figure 7. Surface SEM images of M1 (left) and M2 (right)

CONCLUSIONS

The modification of PES nanofiltration membranes was carried out with addition of different concentrations of AgNPs into the casting solutions. Other important chemicals added in order to improve NF membranes morphology, hydrophilicity and porosity were non-ionic surfactant of Pluronic F108 and PEG. M2 membrane with 0.05 wt.%, 2.0 wt.% and 2.0 wt.% of AgNPs, Pluronic F108 and PEG, respectively showed the highest pure water permeation (PWP), flux and salts rejection performance and were consistent with the obtained SEM images which show better morphological characteristics of M2 in comparison to the other fabricated membranes. Addition of AgNPs in M2, M3 and M4, in comparison to M1 (0 wt.% AgNPs) resulted in high pure water permeation (PWP), flux and salt rejection which indicates improvement of NF membrane performance with the addition of nanoparticle material in membrane formulation.

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REFERENCES

1. S. W. Lin, S. P Sicairos and R. M. F Navarro, J. Mex. Chem. Soc. **51**(3), 129-135 (2007).
2. M. A. Ahmadi, S. Zendehboudi, A. Shafiei and L. James, Ind. Eng. Chem. Res. **51** , 9894-9905 (2012).
3. C. Zhao, J. Xue, F. Ran and S.Sun, Prog. Mater Sci. **58**, 76-150 (2013).
4. M. Sile-Yuksel, B. Tas, D. Y. Koseoglu-Imer and I. Koyuncu, Desalination **347**, 120-130 (2014).
5. C. H. Loh, R. Wang, L. Shi and A. G Fane, J. Membr. Sci. **380**, 114-123 (2011).
6. L. Y. Ng, A. W. Mohammad, C. P. Leo and N. Hilal, Desalination **308**, 15-33 (2013).
7. S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh and M. Beygzadeh, Desalination **349**, 145-154 (2014).
8. M. Safarpour, V. Vatanpour, A. Khataee and M. Esmaeili, Sep. Purif. Technol. **154**, 96-107 (2015).
9. S. Wongchitphimon, R. Wang, R. Jiratananon, L. Shi and C. H. Loh, J. Membr. Sci. **369**(1-2), 329-338 (2011).
10. S. M. Hosseini, E. Bagheipour, A. R Hamidi, A. R. Moghadassi and S. S. Madeini, Journal of the Iranian Chemical Society **13**(10), 1749-1758 (2016).
11. V. Vatanpour, M. Esmaeili and M. H. D. A. Farahani, J. Membr. Sci. **466**, 70-81 (2014).