



Performance Study of Cellulose Acetate Blended Polyvinylchloride Membranes

Pawan Kumar and Vijay Laxmi Yadav†

Department of Chemical Engineering and Technology, IIT-BHU, Varanasi-221005, Uttar Pradesh, India

†Corresponding author: Vijay Laxmi Yadav

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 08-05-2019
Accepted: 21-06-2019

Key Words:

Polyvinyl chloride
Cellulose acetate
Antifouling membrane
Alcohol water mixture

ABSTRACT

In this paper, polymeric membranes were prepared by uniformly dispersing the cellulose acetate, polyethylene glycol and polyvinyl pyrrolidone particles in a polyvinyl chloride matrix for resolving the demand for azeotropic mixture separations. The polymeric membranes were characterized using SEM, FTIR and XRD analysis. The results show that the blending of cellulose acetate and plasticizer diethyl phthalate significantly improved the separation performance of the membranes. The selectivity was increased by adding cellulose acetate up to 2% wt and polyethylene glycol 1% wt. Pervaporation setup was used to separate azeotropic mixture using the prepared membrane. The optimum results were obtained for dehydration of alcohol where the composition plasticizer was 0.5% wt. Based on the findings of the research, it was observed that the PVC membrane can be modified with CA and PEG due to their hydrophobic nature. The results show that the synthesized membrane can be used for removal of water from alcohol.

INTRODUCTION

In the present scenario, the most established membrane separation processes are reverse osmosis, microfiltration, ultra-filtration, and electro dialysis. Except them, two new growing industrial processes are gas separation and pervaporation for separation of an azeotropic mixture (Qureshi 2016). Pervaporation is among the least studied of all membrane separation processes (Pramanik 2017). The work herein has the motive to show the effect of fabrication conditions on membrane performance. The work is mainly focused on the preparation of hydrophobic membranes for the separation of ethanol water mixture. In recent decades, membranes have occupied a major role worldwide in chemical technologies because of a vast diversity of separations can be done by membranes such as separation of gaseous mixtures, filtration of particles from solutions, even membrane are separating close boiling liquids from each other, to name a few (Yamamoto 2017). There is a large number of industries in which such separations are carried out on a large scale such as pharmaceutical, food science and chemical processes (Ayman 2012).

This paper is concerned with the advanced development of polymeric membranes for pervaporation by solution casting method (Sadri 2017). All membranes were prepared using a phase inversion process. Early research was focused on the development of viable membranes (Han 2017 and Zhao 2017).

By the start of the 20th-century, membranes became popular and by the late 1960s onwards many improvements also started in the field of dialysis in medicine and controlled drug delivery by the membranes. This led to the development of microfiltration, ultrafiltration, reverse osmosis and electro dialysis during the 1970's (Chun 2016). Last two decades of the 20th century showed the development of gas separation and pervaporation membrane technologies and current membrane industries took its shape (Imbrogno 2017 and Gu 2016).

A variety of research has been done on the preparation of membranes using polyvinylchloride (PVC) because of their flexibility in operation, durability and better performance and resistance to chemicals. PVC membranes are hydrophobic in nature (Bandi 2016, El-Gendi 2012 and El-Gendi 2014). Commonly, PVC is one of the most common and easily available polymers because of its low price which is less than 1/10 of most common commercial polymer for membrane, i.e. PVDF polymer. Hence, PVC is a major concern for researchers for membrane preparation as it is very competitive to other polymers (Mokhtari 2016).

The objective of this study was to prepare a suitable blend of PVC/CA/PEG membrane for separation of alcohol from an alcohol-water mixture by non-solvent induced phase inversion technique. The prepared membranes were characterized with SEM, X-ray diffractometer and Fourier

Table 1: Polymeric membrane composition for PVC/CA, for different samples of (S-1 to S-4) membrane (weight percentage).

	PVC %	CA %	PEG %	THF %	Plasticizer %
S-1	18	0	2	80	0
S-2	16	2	2	80	0
S-3	15	3	2	80	0
S-4	15	2.5	2	80	0.5

Table 2: Performance of different membranes for separation of ethanol-water.

Membrane	Product Flux for feed conc. 15% alcohol (kg.m ⁻² hr ⁻¹)	Product Flux for feed conc. 30% alcohol (kg.m ⁻² hr ⁻¹)	Product Flux for feed conc. 45% alcohol (kg.m ⁻² hr ⁻¹)
S-1	5.93	5.8	5.88
S-2	4.88	4.99	5.02
S-3	3.773	3.01	3.134
S-4	2.5	2.62	2.53

Table 3: Thickness of prepared membrane samples.

Membrane	Thickness (mm)
S-1	0.41
S-2	0.14
S-3	0.24
S-4	0.30

transform infrared (FTIR) (Oh & Jang 2016). Performance of lab made membranes was investigated by treating a sample of an alcohol-water mixture with different concentration.

MATERIALS AND METHODS

Materials

Polyvinylchloride (PVC) the base polymer, cellulose acetate (CA), polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) were purchased from Sigma Aldrich. Tetrahydrofuran (THF) was used as a solvent and was purchased from Spectrochem, Mumbai. Absolute alcohol was used to check the performance of the membranes.

Preparation of Membranes

Blended PVC/CA/PVP membranes were prepared by the phase inversion process (Saljoughi et al. 2009). The known amounts of polymers were dissolved in NMP and compositions of samples are shown in Table 1. After this, the solution was stirred for 12 hr. The solution of polymer was cast on a glass plate, and glass plate was subsequently dipped in a non-solvent bath of deionized water. The water was changed three times for complete exchange of solvent THF. And finally, the membrane was dried in the oven at 50°C and then used further.

Membrane Characterization

Surface morphology of prepared membrane samples was investigated by scanning electron microscopy (SEM). Samples were pre-coated with gold to provide electrical conductivity. The instrument used for the purpose was EVO - Scanning Electron Microscope MA15/18, Carl Zeiss Microscopy Ltd., USA. The crystalline or amorphous nature of polymeric membranes was investigated using X-ray diffractometer (XRD, model - EDS System, Carl Zeiss Microscopy Ltd., USA) with a scanning rate of 5° per minute in the range of 0° to 70° (2θ). The functional changes in the polymeric membranes were analysed in the transmittance mode from 4000 to 400 cm⁻¹ wavelength range using Fourier Transform Infrared Spectroscopy (FTIR) Varian 1000, USA.

A lab scale dead end pervaporation setup was used to study the performance of samples using an alcohol water mixture. Performance of membrane was expressed in terms of permeate flux.

RESULTS AND DISCUSSION

Thickness of Membrane

The thickness of the different membrane samples, measured using digital Vernier callipers, is given in Table 3. The

Table 4: Wavelength for cellulose acetate group.

Wavelength cm^{-1}	Chemical bond
2918.9-3406.1	-OH
1633.3-1738.2	C=O
1370.9-1489.7	CH_3
1769.7	-CH
1044.9	C-O-C
669.3	R-COH

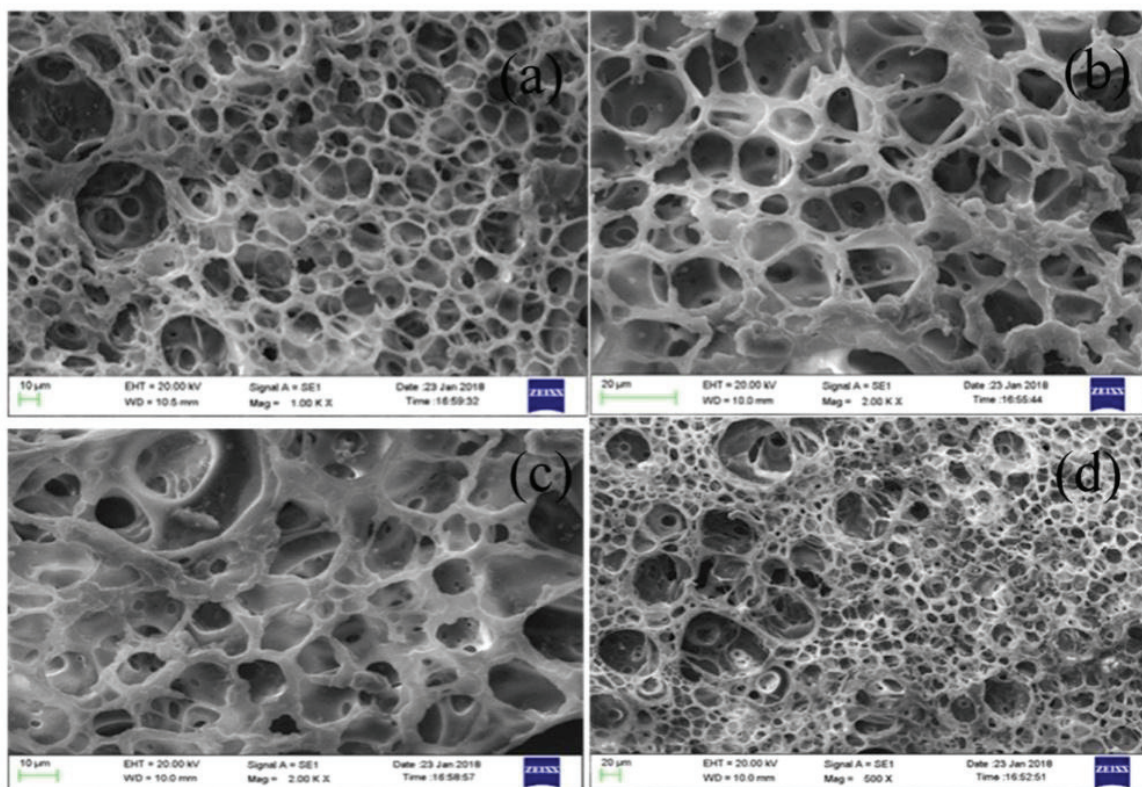


Fig. 1: SEM images of prepared PVC membranes (a)- sample S-1, (b)- sample S-2, (c)- sample S-3, (d)- sample S-4.

thickness of the membrane increased when the amount of the cross linker was increased. This occurs due to high bonding between cross linker and polymer. It is seen that as the amount of cross-linking agent is increasing, membrane thickness is also increasing due to the formation of an intermediate layer of fillers due to the polymerization of cross linker.

Membrane Morphology

SEM micrographs of different samples have been shown in Fig. 1(a-d). SEM images show a cross section of the (S-1) membrane. Expected asymmetric pores are observable in the entire surface as the CA was added to the system. At the same

time S-2 shows different surface pattern. It was seen in the image of S-2 that surface become rougher and pores become denser as the result of blending. Saljoughi et al. (2009) had also shown similar changes. Similarly, by addition of more CA in S-3, number of pores decreased and it was visible in SEM image. In S-4, plasticizer was added to see its effect on the surface. It was seen that by addition of plasticizer, pores became large which in turn increased the flux through the membrane and this phenomenon was verified by performance studies where S-4 shown better flux.

FTIR Analysis

Membranes were further characterized by Fourier Transform

Infrared (FTIR) spectroscopy in the range 4000-400 cm^{-1} to know the functional groups present in the samples to verify the formation of desired composites. The membrane samples (S1 - S4) were tested for comparison and the result is shown in Fig. 2. The peaks corresponding to 2520 cm^{-1} for sample S-1, 2640 cm^{-1} for sample S-2, 2750 cm^{-1} for sample S-3, 2610 cm^{-1} for sample S-4 and at 2595 cm^{-1} for sample S-4 corresponding to C-H stretching (Saljoughi et al. 2009).

Functional groups and their peaks which are common for CA are given in Table 4. A peak at 1470 cm^{-1} was observed (except in sample-1) corresponding to $-\text{CH}_2$ bonding. The C-Cl stretching was indicated by the 4 peaks at 727 cm^{-1} , 685 cm^{-1} , 715 cm^{-1} and 750 cm^{-1} for the sample S-1, S-2, S-3, and S-4 respectively. The effect of adding PEG was observed in sample-1 at peak 683 cm^{-1} indicating that PEG mostly influences the membrane structure.

After blending of PVC with CA and PEG, a shift was observed for PVC and CA peaks.

X-Ray Diffraction (XRD) Analysis

The crystalline and amorphous character of the membrane was studied by X-ray diffraction measurement and has been

shown in Fig. 3. We can see from Fig. 3(a) of sample-1 the XRD patterns two peaks are observed. Here peaks are seen at a 2-theta value of 17° and 26°. Broad peaks appeared at 26° and smaller peak appeared at 17°.

Further, from Fig. 3(b) of sample-2, we can also see that when we increase the amount of PVC again, we observed 2 peaks at a 2-theta value of 27° and 38°, but the peak corresponding to 27° is more intense and higher. These peaks are sharper than sample-1 that can be attributed to the involvement of cellulose acetate. Such results are also observed by Saeki et al (2013) while preparing poly amide membrane with similar procedure.

From the Fig. 3(c) of sample-3, we observe the same XRD pattern as in the graph of sample-2. There are 2 peaks at a 2-theta value of 27° and 38°, but this time high peak appears at 27° and a smaller peak at 38°. The intensity of peaks is higher than those of sample-2. This can be due to the addition of 2% PEG as a pore creator.

From the Fig. 3(d) of sample-4 in which 0.5% plasticizer was also added to increase the elastic nature of the sample. In this case, it was observed same XRD pattern as in Fig. 3(b) of sample-2 and in Fig. 3(c) of sample-3. In this, we

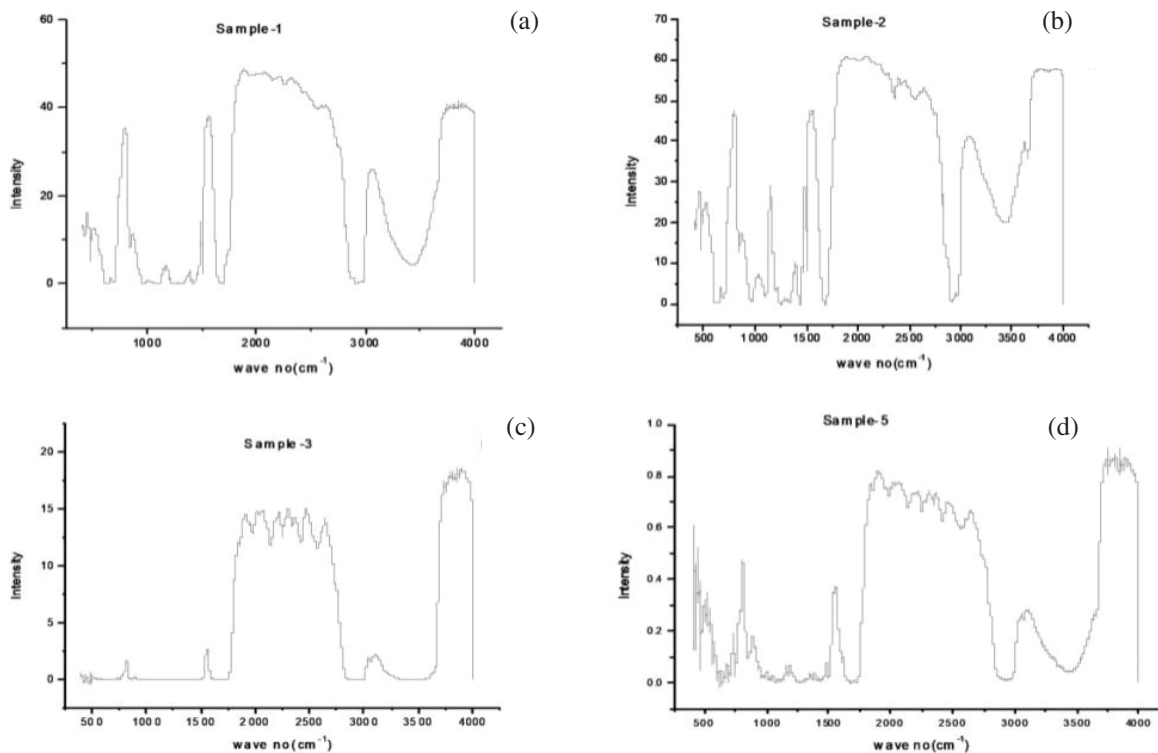


Fig. 2: FTIR spectra of prepared membranes (a) sample S-1, (b) sample S-2, (c) sample S-3, (d) sample S-4.

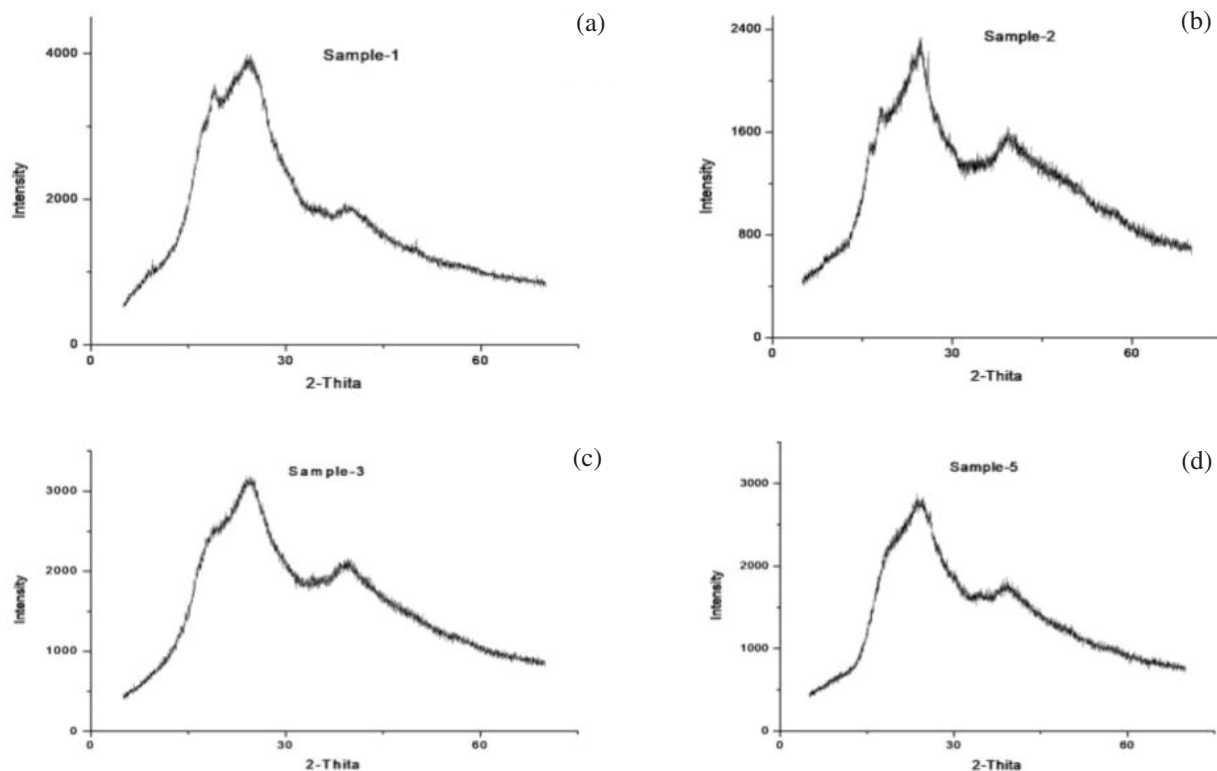


Fig. 3: XRD patterns for different samples.

observed 2 peaks at 26.5° and 33° , but this time high peak appears at 26.5° , and smaller one appears at 33° , but the intensity of peaks is higher than in Fig. 3(b) of sample-2 and in Fig. 3(c) of sample-3. This can be due to the addition of 0.5% plasticizer to increase elasticity.

Membrane Performance

In order to check the performance of the membrane, the ethanol-water mixture was used as the feed. Several compositions of the ethanol-water mixture were used to measure the flux of ethanol across the membrane to study the performance of the prepared membrane. Table 2 shows the observations regarding the flux of product for various samples.

From Table 2 we can say that the total flux through the membrane is in the order of $S-1 > S-2 > S-3 > S-4$. In S-1, equal amount of PVC and PEG were involved and porosity of this membrane is highest resulting in maximum flux compared to other membrane samples.

In S-2 (PVC blend with CA and PEG), we observed less product flux compared to S-1. This can be due to the fact that on increasing the amount of PVC and adding one more additive PEG, the porosity goes down.

In the preparation of S-3 flux of product again decreases and is less than S-2. This can be due to the fact that on adding more polymer, particles started aggregating and, pore would be denser, hence the resulting flux decreases. When we use S-4 membrane for pervaporation of given feed, we observed that the flux decreases but the change in amount was less than S-2 and S-3. In S-4 membrane we have added a plasticizer to enhance the elasticity.

CONCLUSION

PVC/CA/PEG and PVP blended membrane were successfully prepared via wet phase inversion technique using different concentrations of the component polymers. The following conclusions can be drawn from the above work: From SEM analysis membranes were found to be a dense and asymmetric membrane. Characterization results indicate that membrane S-4 is the best membrane among the prepared membranes S-1 to S-4. The durability test of membrane S-4 was conducted, and the membrane performance was approximately constant and stable over 20 days. FTIR and XRD analysis showed the proper formation of the composite by the process and by performance studies, it was observed

that membrane containing PVC, CA and plasticizer has the highest flux, so the blend of sample 4 was optimum according to our study for separation of alcohol water mixture.

REFERENCES

- Ayman, E.G., Heba, A. and Sahar A. 2012. Construction of ternary phase diagram and membrane morphology evaluation for polyamide/formic acid/water system. *Australian J. Basic App. Sci.*, 6(5): 62-68.
- Bandi, C.S., Uppaluri, R. and Kumar, A. 2016. Global optimization of MSF seawater desalination processes. *Desalination*, 394: 30-43.
- Chun, Y., Zaviska, F., Kim, S.J. and Mulcahy, D. 2016. Yang, E., Kim, I. S. and Zou, L., Fouling characteristics and their implications on cleaning of a FO-RO pilot process for treating brackish surface water. *Desalination*, 394: 91-100.
- El-Gendi, A., Ali, S.S., Ahmed, S.A. and Talaat, H.A. 2012. Development of membrane blend using casting technique for water desalination. *Membrane Water Treatment*, 3(3): 201-209.
- El-Gendi, A., Deratani, A., Ahmed, S.A. and Ali, S.S. 2014. Development of polyamide-6/chitosan membranes for desalination. *Egyptian J. Petro.*, 23(2): 169-173.
- Gu, H., Rahardianto, A., Gao, L.X., Christofides, P.D. and Cohen, Y. 2016. Ultrafiltration with self-generated RO concentrate pulse backwash in a novel integrated seawater desalination UF-RO system. *J. Memb. Sci.*, 520: 111-119.
- Han, S., Rhee, Y.W. and Kang, S.P. 2017. Investigation of salt removal using cyclopentane hydrate formation and washing treatment for seawater desalination. *Desalination*, 404: 132-137.
- Ibrahim, S.M., Nagasawa, H., Kanezashi, M. and Tsuru, T. 2015. Robust organosilica membranes for high temperature reverse osmosis (RO) application: Membrane preparation, separation characteristics of solutes and membrane regeneration. *J. of Memb. Sci.*, 493: 515-523.
- Imbrogno, J., Keating IV, J.J., Kilduff, J. and Belfort, G. 2017. Critical aspects of RO desalination: A combination strategy. *Desalination*, 401: 68-87.
- Mokhtari, H. and Sepahvand, M. 2016. Thermoeconomic and exergy analysis in using hybrid systems (GT+ MED+ RO) for desalination of brackish water in Persian Gulf. *Desalination*, 399: 1-15.
- Oh, J.H. and Jang, A. 2016. Application of chlorine dioxide (ClO₂) to reverse osmosis (RO) membrane for seawater desalination. *J. Taiwan Inst. Chem. Engg.*, 68: 281-288.
- Pramanik, B.K., Gao, Y., Fan, L., Roddick, F.A. and Liu, Z. 2017. Antiscalcing effect of polyaspartic acid and its derivative for RO membranes used for saline wastewater and brackish water desalination. *Desalination*, 404: 224-229.
- Qureshi, B.A., Zubair, S.M. 2016. Exergetic efficiency of NF, RO and EDR desalination plants. *Desalination*, 378: 92-99.
- Sadri, S., Ameri, M. and Khoshkhoo, R.H. 2017. Multi-objective optimization of MED-TVC-RO hybrid desalination system based on the irreversibility concept. *Desalination*, 402: 97-108.
- Saeki, D., Nagao, S., Sawada, I., Ohmukai, Y., Maruyama, T. and Matsuyama, H. 2013. Development of antibacterial polyamide reverse osmosis membrane modified with a covalently immobilized enzyme. *J. Memb. Sci.*, 428: 403-409.
- Saljoughi, E. and Mohammadi, T. 2009. Cellulose acetate (CA)/polyvinylpyrrolidone (PVP) blend asymmetric membranes: Preparation, morphology and performance. *Desalination*, 249(2): 850-854.
- Yamamoto, K., Koge, S., Gunji, T., Kanezashi, M., Tsuru, T. and Ohshita, J. 2017. Preparation of POSS-derived robust RO membranes for water desalination. *Desalination*, 404: 322-327.
- Zhao, Y., Zhang, Z., Dai, L., Mao, H. and Zhang, S. 2017. Enhanced both water flux and salt rejection of reverse osmosis membrane through combining isophthaloyl dichloride with biphenyl tetra acyl chloride as organic phase monomer for seawater desalination. *J. Memb. Sci.*, 522: 175-182.