

## Integral Membrane Properties of Polysulfone/Chitosan/Polyvinyl Alcohol Blend Incorporated with Rice Husk Ash Silica Gel

Nur Syazwanie Izzati Chik and Norin Zamiah Kassim Shaari\*

School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Selangor, Malaysia

\* Corresponding author:

email: norinzamiah@uitm.edu.my

Received: August 11, 2022

Accepted: March 13, 2023

DOI: 10.22146/ijc.76999

**Abstract:** In this study, silica gel was extracted from rice husk ash using a modified acid-leaching process. The gel was then characterized using an X-ray Diffractometer (XRD) and an X-ray Fluorescence (XRF). At different loadings of 0, 0.05 and 0.10 wt.%, silica gel was used as a cross-linker in the membrane formulation. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used to characterize the membranes, while their performance was determined by pure water flux. XRD and XRF results revealed that the gel contained 76.85% silica. The presence of silica gel in membranes results in optimal water flux, indicating that the membranes have achieved good integral stability via the cross-linking process. Based on these positive findings, the applications of the membranes in the water-oil separation process will be evaluated in future work.

**Keywords:** cross-linking; integral membrane; rice husk ash; silica gel

### ■ INTRODUCTION

The world's rice consumption will continue to rise with the number of consumers. Because rice husk waste is abundant, some alternatives to add its value are being explored. The composition of rice husk (RH) comprises 70–80% cellulose and lignin, with 20–30% silica, alkali, and trace elements. RH has a high energy content of 16,720 kJ kg<sup>-1</sup>, making it suitable for burning fuel or post-combustion [1]. When RH is burned between 350 and 750 °C, an amorphous shape of silica is formed, whereas a crystalline shape is formed when it is burned above 800 °C [2]. The yield of the ash is 25% when RH is burned.

The rice husk ash (RHA) is composed of 85–95% amorphous silica and a trace amount of alkali oxide [3]. The percentage of silica in rice varies according to its origin and the process of burning the husk. RHA is used in ceramics, construction, chemicals, and electronics because it increases the material's workability and mechanical properties [4-5]. Aside from that, it can be used as a filler for membranes, adsorbents, photoluminescent substances, and a filler for activated carbons [5]. RHA's popularity stems from the fact that it is both environmentally friendly and inexpensive.

On the other hand, silicate from rice husk ash can act as a cross-linker if incorporated into a membrane. This silica is introduced during the polymer-making process as a cross-linking reaction in which the polymer chain forms a network structure as a stabilization process during the reaction [6]. Inorganic silica gel is one of the inorganic materials that has been applied nowadays in wastewater treatment as a membrane for heavy metal removal and dyes. Having a structure with high porosity, hydrophilicity, and high activity makes the structure such a sponge for better adsorption. Silica gel is widely used because the pore structure inside the silica gel is easy to control, has strong selectivity, and high stability, and consists of silanol hydroxyl group. The silanol group is formed when the silicate tetrahedrons are condensed using oxygen as their binding site to generate the siloxane bond (Si–O–Si). Thus, the silanol group is originated from the siloxane bond when the synthetic silica is extracted from RHA. Moreover, this silica gel also increases the power of adsorption and selectivity to heavy metal ions [6].

There are two methods of extraction process: acid leaching and alkali leaching. Acid leaching is the most widely used method because it can produce silica at high

purity, where the silica has a large surface area for adsorption and with amorphous and mesoporous particles [7]. The amorphous structure is highly preferred for silica as the solubilities are enhanced as compared to the crystalline structure. This property is important in the membrane-making process as a homogeneous solution can be formed [8].

Acid leaching is the most common silica extraction method for RHA. This method is simple and does not require heating to a high temperature. RHA is cleaned of metal impurities with HCl before being treated with NaOH to produce sodium silicate. It was then followed by titration with HCl to form silica gel. This amorphous substance was derived from the dehydration process of silicate tetrahedrons to form a nanometer size of substance with siloxane bonds (Si–O–Si). In the membrane-making process, a study was reported on incorporating tetraethylorthosilicate as the silica nanoparticle into the blend polymer of polyvinyl alcohol/polyethylene glycol/glycerol [9]. It was found that the crosslinking process through the sol-gel method has improved the thermal and mechanical stabilities of the membranes. The sol-gel method involves the hydrolysis of silica, and the subsequent condensation process to form a covalent bond.

Aside from improving its properties, the incorporation of silica during the membrane formulation can combat the fouling and improve the hydrophilicity of the membrane [10]. By improving the interconnectivity of pores in the top layer and sub-layer of the membrane, these additives can avoid the formation of macro-voids, improve the flux, and increase the rejection of the respective pollutants [11-13]. According to Harun et al. [14], silica is chemically resistant and thermally stable. Furthermore, its high hydrophilicity manages to lessen fouling mechanisms by enhancing water permeation [14]. Previously, researchers investigated the use of tetraethylorthosilicate as a cross-linker in a composite hybrid membrane with polysulfone membrane as the support membrane. Results from antifouling evaluation revealed that the membranes exhibited good antifouling behavior with the use of humic acid as the foulant model with the additional advantage of high thermally stable and

high adsorption towards heavy metal [15].

The purpose of this study is to examine the outcome of the RHA silica extraction process using a modified acid-leaching method, as well as to evaluate the effect of the silica gel addition in the membrane formulation on the characteristics of the fabricated membranes.

## ■ EXPERIMENTAL SECTION

### Materials

Polyvinyl alcohol (PVA, 87–89% hydrolyzed with a molecular weight average of 85,000–124,000) and polysulfone (PSF with a molecular weight of 22,000) were obtained from Sigma-Aldrich (M) Sdn Bhd, Malaysia. Aman Semesta Enterprise in Malaysia supplied the chitosan (CS). Merck Sdn. Bhd., Malaysia, supplied the 1-methyl-2-pyrrolidone (NMP) and polyethylene glycol 400 used in this study. R&M Chemicals, Malaysia, supplied the hydrochloric acid (HCl, 37% purity) and dimethyl sulfoxide. BT Science Sdn. Bhd. in Malaysia supplied the rice husk ash. Deionized water and distilled water were obtained from the UiTM Shah Alam Chemical Laboratory in Malaysia.

### Instrumentation

Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FTIR) instrument with Model Spectrum 400 was utilized to identify the emergence of functional groups in the silica gel as well as in the membrane. The analysis produces an infrared absorption spectrum, which identifies the presence of chemical bonds in the molecule. The wavelength was analyzed between 400 and 4000  $\text{cm}^{-1}$  [16]. For the analysis of membrane surface morphology, a Field-Emission Scanning Electron Microscopy (FESEM) brand Joel: Model JSM-7600F was used. The pattern of the RHA silica gel was evaluated using a Rigaku X-ray Diffractometer: Model D/Max200V/PC with an accelerated voltage of 40 kV and a current of 30 mA. At a rate of 5°/min, the diffraction angle ( $2\theta$ ) was scanned from 10 to 80° [17]. X-ray Fluorescence Spectrometer (XRF) by Philip was utilized for the analysis of the extracted silica gel. The membrane filtration rig, which

uses nitrogen gas for purging, was used in the filtration process. The tools used for this study were a hot plate, magnetic stirrer, electrical balance, glassware, aluminium foil, filter paper, and pH paper.

## Procedure

### Silica extraction from RHA

The extraction method was adapted from de Lima et al. [17] with some modifications on the amount of raw RHA used and some parameters such as temperature and time. To 250 mL of distilled water, 25 g of raw RHA was added. To remove metal impurities, 8 g of HCl was added to the mixture. This is known as the pre-cleaning procedure. For 1 h, the solution was heated to 90 °C with continuous stirring at 650 rpm before it was left to cool overnight at room temperature. The filtration process was conducted through Smith 102 filter paper. The cleaned RHA was labeled on the permeated liquid. The permeated liquid was poured into a solution of 1 M NaOH with 250 mL volume. The mixture was heated at 80 °C and swirled at 600 rpm for 1 h in an alkaline leaching process. After it was left overnight, another filtration process was performed by using Smith 102 filter paper. The brownish liquid obtained from the filtration process was known as sodium silicate ( $\text{Na}_2\text{SiO}_3$ ). The liquid has a pH of 14 after being tested with universal pH paper. For the gelling process, one normality of HCl was prepared. The titration using the HCl was conducted on the  $\text{Na}_2\text{SiO}_3$  until it reached pH 7, at which point it solidified into a gel texture. The gel was left to mature for 24 h before it was then vigorously stirred with a magnetic stirrer at 1500 rpm to break it down into smaller sizes. It was then washed with

400 mL of distilled water. The washing procedure was repeated four times until the gel was clear (whitish). This step was taken to remove sodium chloride (NaCl) to obtain high-purity silica oxide ( $\text{SiO}_2$ ) [17-19]. The reaction mechanism involved in the production of silica gel is depicted in Fig. 1. Fig. 2 depicts images of mature and washed silica gel, respectively. XRD, XRF, and FTIR were then used for the characterization of the silica gel.

### PVA and CS solutions preparation

A 10 wt.% PVA solution was prepared by dissolving 10 g of PVA powder into 90 g of dimethyl sulfoxide for 4 h at 90 °C and 400 rpm stirring rate. After that, the solution was left to cool down. To make the CS solution, 0.02 g of CS was mixed with 99.98 g of 2 wt.% aqueous acetic acids, followed by heating at 90 °C for 4 h and at 400 rpm of stirring. The mixture was left to cool down before mixing [20].

### Cross-linking process of PVA/CS solution

Both prepared PVA and CS solutions were mixed with 400 rpm stirring for 7 h while heated to 60 °C. Silica gel was poured into the mixture at a concentration of 0 to 0.10 wt.% of the total mixture [14]. As a catalyst, 1 mL of HCl 37% was added. The formulations of each membrane are shown in Table 1 [15,20]. Fig. 3 depicts the cross-linking reaction from the sol-gel method between the silicate from RHA gel and the hydroxyl group from PVA.

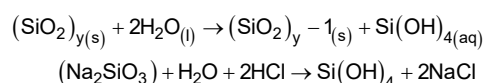


Fig 1. Reaction mechanism of silica gel [18]

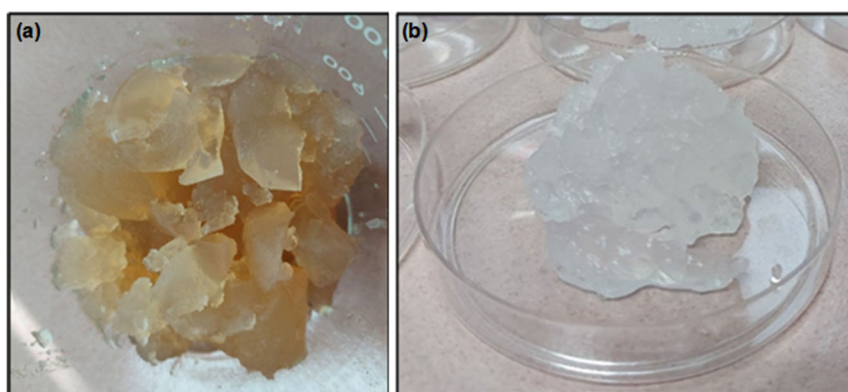
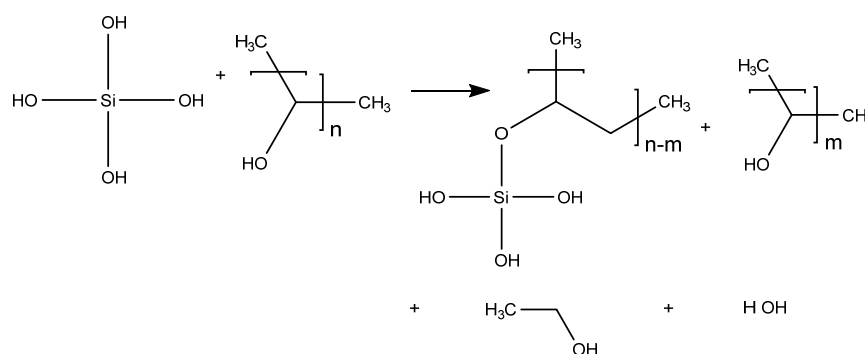


Fig 2. (a) Mature and (b) washed RHA silica gel

**Table 1.** The formulations of membranes

Membrane code	Hybrid solution			
	PVA solution (g)	CS solution (g)	Silica gel (wt.%)	HCl (mL)
MA	50.00	50.00	0.00	1.00
MB	50.00	50.00	0.05	1.00
MC	50.00	50.00	0.10	1.00

**Fig 3.** Reaction mechanism between RHA silica gel and a hydroxyl group from PVA [20]**Table 2.** Membrane formulations

Membrane	PSF solution (g)	Hybrid solution (g)
MA	50.00	1.00 (without silica)
MB	50.00	1.00 (0.05 wt.% silica)
MC	50.00	1.00 (0.10 wt.% silica)

### Polysulfone (PSF) solution preparation

To make 13 wt.% PSF solution, 13 g of PSF beads were dissolved in 82 g of NMP, followed by adding 5 g of PEG 400. For approximately 6 h, the solution was heated at 60 °C and stirred at 400 rpm. The solution was left at room temperature before the membrane solution was prepared [15].

### Membrane preparation

A 50 g PSF solution was mixed with one gram of each prepared hybrid membrane solution shown in Table 1. For 3 h, a stirring was set at 700 rpm while the mixture was being heated at 80 °C. The formulation for each membrane is shown in Table 2. For the membrane film-making process, the membrane solution was spread to a thickness of 100 μm with a Baker's Film Applicator on a glass plate. The plate was submerged in a water-containing coagulation bath for 24 h to solidify. This method was called the phase inversion method. Then, the film of the membrane was allowed to cure for 1 d at room temperature [20]. The films were characterized by functional groups using FTIR and surface morphology

using FESEM, and the performance was checked through pure water flux.

### RHA silica gel yield calculation

Eq. 1 was used to determine the yield of RHA silica gel after the washing process;

$$Y_g = \frac{c}{m} \times 100\% \quad (1)$$

where *m* represents the weight of mature silica gel, *c* is the weight of washed silica gel, and *Y<sub>g</sub>* is the yield of silica gel (%) after washing [21].

### Analysis of water flux

A dead-end filtration rig was used for the water flux evaluation, which was conducted at room temperature. The apparatus was linked to a compressed nitrogen gas cylinder, which applied pressure to the feed solution. The filtration through the membrane was performed at 6 bars for 60 min, with sampling every 15 min. The flux was determined through the collected volume of the permeate solution. For each formulation, three membrane samples were tested before the average reading was recorded. The membrane was cut into a circular shape with an area of  $0.196 \times 10^{-2} \text{ m}^2$ . Eq. 2 was used to calculate the permeate flux;

$$J_p = \frac{Q_p}{A \Delta t} \quad (2)$$

where  $J_p$  is the permeate flux ( $L\ m^{-2}h^{-1}$ ),  $Q_p$  is the volume of permeate (L),  $A$  the effective membrane area ( $m^2$ ), and  $\Delta t$  is the sampling time (h) [22].

## ■ RESULTS AND DISCUSSION

### RHA Silica Gel Analysis

Fig. 4 depicts the result from the XRD analysis. Based on the image, the silica gel shows an amorphous structure without the presence of NaCl because no crystalline peaks were observed in the range of 30 to 60° [19]. This result shows a similar pattern to the one obtained from the previous research by de Lima et al. [17], where the modified extraction process successfully extracted a high amount of  $SiO_2$  [17]. It could be concluded that the washing method in this modified method has been carried out efficiently to remove all the NaCl. NaCl in the silica gel should be avoided because it may interfere with the cross-linking reaction in the membrane-making process [18].

A further investigation of the composition of the silica gel was performed through XRF analysis. Table 3 shows that the gel has 76.85% silica with 0.55% Na and 0.72% Cl. The remaining 21.88% of the total composition could be oxides and metal impurities. Although the washing process can remove all the NaCl, it fails to remove the metal impurities. Setyawan [19] discovered that RHA extraction yielded 86.17%  $SiO_2$ , and the results

were relatively high in comparison to this finding. The reason could be due the RHA was obtained from different sources in local areas.

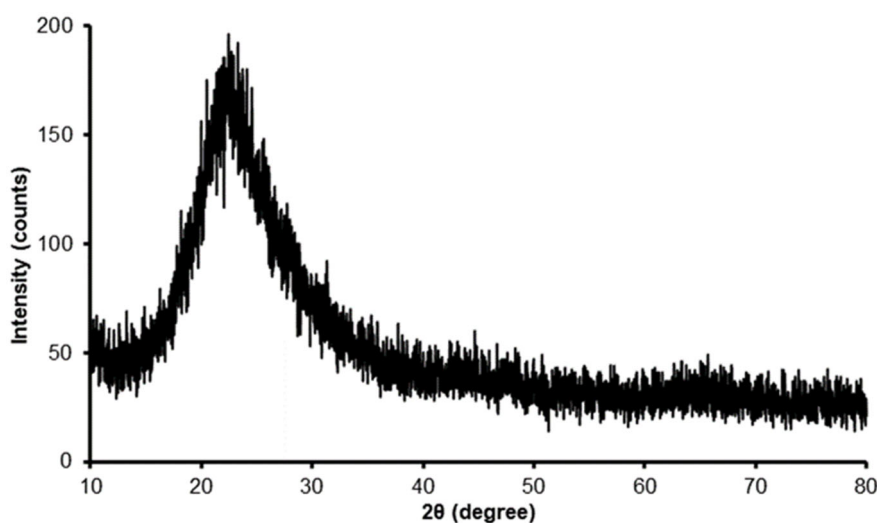
FTIR analysis of the RHA silica gel was performed in the 400–4000  $cm^{-1}$  range. The spectra in Fig. 5 can identify a few major chemical groups. The strong and broad absorbance of the silanol O–H group stretching at peak 3296  $cm^{-1}$  and symmetric stretching vibration band at peak 1635  $cm^{-1}$  indicates another O–H group from water [6,23–24]. Si–O–Si absorption band was discovered at 1082  $cm^{-1}$  [24–26].

### Characteristics of Integral Membrane

The FTIR spectra of membranes MA, MB, and MC are shown in Fig. 6. The peaks of the three membranes are primarily composed of PSF/PVA/CS, with silica gel incorporated as a cross-linker in the formulations of MB and MC. Overall, the fingerprints of MB and MC differed only slightly due to the appearance of small peaks ranging from 400 to 4000  $cm^{-1}$ . In the 2800–3600  $cm^{-1}$  range, it

**Table 3.** The elements of silica gel

Element	Percentage (%)
Si	76.85
Na	0.55
Cl	0.72
Others	21.88



**Fig 4.** X-ray diffraction pattern of RHA silica gel

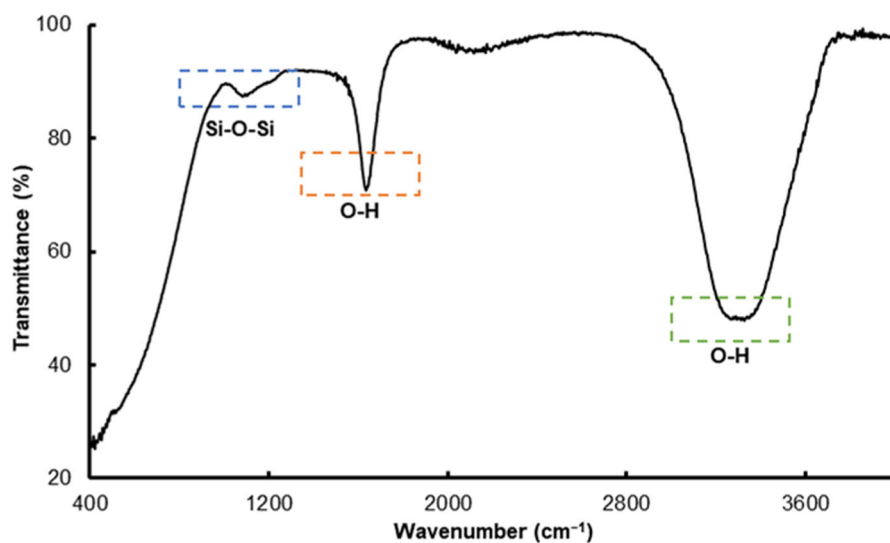


Fig 5. FTIR spectra of RHA silica gel

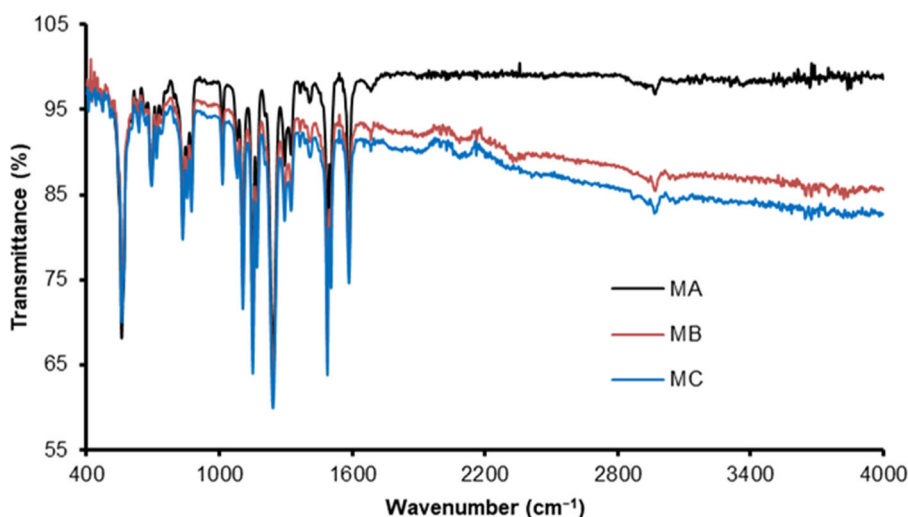


Fig 6. FTIR spectra of membranes

corresponded to the silanol O-H groups of silica gel that have overlapped with hydroxyl groups (O-H) of PVA for MB and MC. The spectra revealed that all membranes had C-H stretching that overlapped with amine bands at a peak around  $2969\text{ cm}^{-1}$ , and the peak at  $1600\text{ cm}^{-1}$  also corresponded to O-H groups [16,20]. The vibration modes of C=O and C-O bonds were coming from the unhydrolyzed vinyl acetate of PVA that was observed between  $1100$  and  $1700\text{ cm}^{-1}$  [16]. The peaks of MB and MC at  $2139$  and  $2156\text{ cm}^{-1}$ , respectively, represent the weak stretching band of C=C alkynes derived from conjugated silica gel [27-28]. The stretching mode of Si-O is usually assigned to the absorption band between  $1000$  and

$1100\text{ cm}^{-1}$  for MB and MC [29], where the crosslinking process to form Si-O-C at  $1107\text{ cm}^{-1}$  resulted in the overlapping to the original C-O bond. Despite being crosslinked by silica, the O-H groups stretching in membranes MB and MC at  $2800$ – $3600\text{ cm}^{-1}$  showed a membrane's hydrophilicity [26].

Fig. 7 depicts the surface morphology of membranes. Based on the images, it was observed that the pore structure of MA was uneven in size and had a larger pore size as compared to MB and MC. Membranes MB and MC had smaller pore sizes and denser surfaces that were caused by the reaction between the polymer blend's O-H group and the Si-O-H of the silica gel [16].

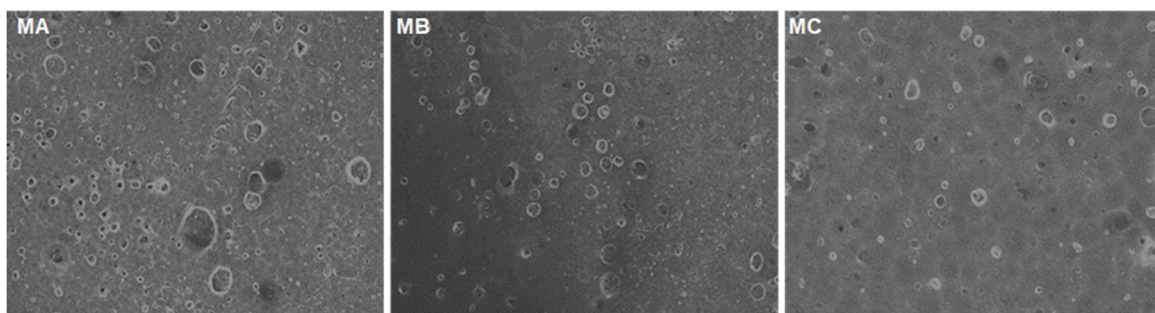


Fig 7. Surface morphology structure of membranes

Observing the surface structure of MB and MC, it was concluded that both membranes had a smooth surface, and no agglomeration was spotted, which proved that the crosslinking process with the silica gel was successful [18].

### Water Flux Analysis

Fig. 8 depicts the pure water flux (PWF) results for MA, MB, and MC after 1 h of filtration. PWF is related to the surface structure of the membrane and its hydration properties, with a constant value of PWF indicating that the membrane porosity remained constant throughout the filtration time [22]. The increment in the water flux indicates changes in the permeable structure of the membrane [21].

According to Fig. 8, the flux for MA continues to increase until 1 h, indicating that there are changes in the pore sizes of the membrane [30]. The membrane must have ruptured, causing the pore size to increase. It was also observed through a visual that the membrane was swollen at the end of the filtration process. Realizing that PVA has an abundance of O–H groups, this situation was attributed to the membrane's lack of integral stability in the absence of a cross-linker such as RHA silica gel [31]. It could be related to Fig. 7 where the structure of the membrane MA was not compact without the cross-linking process, resulting in high water flux and swelling of the membrane.

Different flux patterns were observed in the MB and MC, where the flux began to decrease gradually after 15 min of filtration and continued to decrease until 1 h of filtration time. After 1 h, the fluxes for MB and MC were  $40.7 \text{ L m}^{-2} \text{ h}^{-1}$  and  $26.9 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively. It was

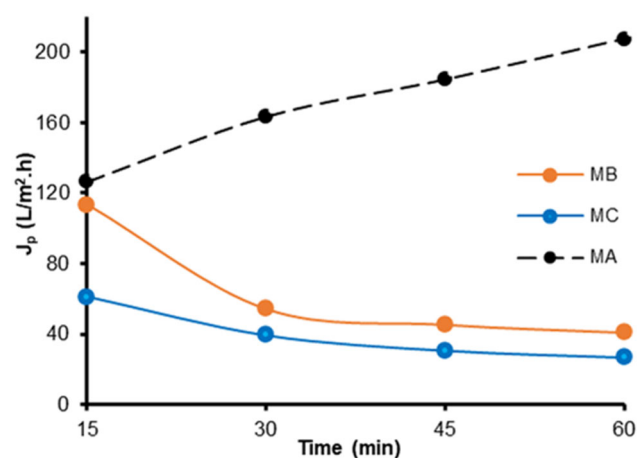


Fig 8. Pure water flux of membranes

observed that there was no pore enlargement on the surface of the membrane after the filtration process. This situation demonstrated that the crosslinking process improved the membrane's structure by providing higher membrane stability [31]. Although the crosslinking reaction utilized the O–H group from the polymer blend, the silica with good hydrophilicity compensated for the effect to ensure membranes MB and MC exhibited good water permeability [26,32]. MC has a lower flux than MB due to an increase in cross-linking degree due to a higher concentration of RHA silica gel added to the membrane formulation.

### CONCLUSION

In conclusion, a modified acid leaching technique was found to successfully extract a significant amount of silica from the rice husk ash. The process also was successful in removing NaCl. Even though only 76.85% silica could be extracted, the incorporation of silica gel

in the membrane formulation had a significant effect in terms of improving the membrane polymer matrix through the cross-linking process, with the added benefit of homogeneous membrane solution being produced. Based on this promising result, additional research will be carried out to evaluate the performance of the membranes in the water-oil separation process.

## ■ ACKNOWLEDGMENTS

The study was supported by Universiti Teknologi MARA (UiTM) through a grant with a file number 600-RMC/GPK 5/3 (119/2020).

## ■ REFERENCES

- [1] Ilochonwu, C.E., Nwajagu, C.O., Onyenanu, I.U., and Nwonye, E.I., 2016, "Effect of Temperature in Extraction of High Purity Amorphous Silica from Rice Husk for Silicon Production" in *EPD Congress 2015*, Eds. Yurko, J.A., Allanore, A., Bartlett, L., Lee, J., Zhang, L., Tranell, G., Meteleva-Fischer, Y., Ikhmayies, S., Budiman, A.S., Tripathy, P., and Fredrickson, G., Springer, Cham, 219–227.
- [2] Rasoul, B.I., Günzel, F.K., and Rafiq, M.I., 2018, "Effect of Rice Husk Ash Properties on the Early Age and Long Term Strength of Mortar" in *High Tech Concrete: Where Technology and Engineering Meet*, Eds. Hordijk, D.A., and Luković, M., Springer International Publishing, Cham, 207–214.
- [3] Hossain, S.K.S., Mathur, L., Bhardwaj, A., and Roy, P.K., 2019, A facile route for the preparation of silica foams using rice husk ash, *Int. J. Appl. Ceram. Technol.*, 16 (3), 1069–1077.
- [4] Todkar, B.S., Deorukhkar, O.A., and Deshmukh, S.M., 2016, Extraction of silica from rice husk, *Int. J. Eng. Res. Dev.*, 12 (3), 69–74.
- [5] You, P.Y., Kamarudin, S.K., and Masdar, M.S., 2019, Improved performance of sulfonated polyimide composite membranes with rice husk ash as a bio-filler for application in direct methanol fuel cells, *Int. J. Hydrogen Energy*, 44 (3), 1857–1866.
- [6] Rohaeti, E., Primadiska, N.R., and Rafi, M., 2020, Silica modified L-lysine as Pb(II) adsorbent, *AIP Conf. Proc.*, 2243, 030020.
- [7] Steven, S., Restiawaty, E., Pasymi, P., and Bindar, Y., 2021, An appropriate acid leaching sequence in rice husk ash extraction to enhance the produced green silica quality for sustainable industrial silica gel purpose, *J. Taiwan Inst. Chem. Eng.*, 122, 51–57.
- [8] Ditzinger, F., Price, D.J., Ilie, A.R., Köhl, N.J., Jankovic, S., Tsakiridou, G., Aleandri, S., Kalantzi, L., Holm, R., Nair, A., Saal, C., Griffin, B., and Kuentz, M., 2019, Lipophilicity and hydrophobicity considerations in bio-enabling oral formulations approaches - A PEARRL review, *J. Pharm. Pharmacol.*, 71 (4), 464–482.
- [9] Shaari, N.Z.K., Abd Rahman, N., Sulaiman, N.A., and Mohd Tajuddin, R., 2017, Thin film composite membranes: Mechanical and antifouling properties, *MATEC Web Conf.*, 103, 06005.
- [10] Swain, B., 2017, Recovery and recycling of lithium: A review, *Sep. Purif. Technol.*, 172, 388–403.
- [11] Jamalludin, M.R., Harun, Z., Basri, H., Yunus, M.Z., and Shohur, M.F., 2013, Performance studies of polysulfone-based membrane: Effect of silica morphology, *Appl. Mech. Mater.*, 372, 8–12.
- [12] Jamalludin, M.R., Harun, Z., Hubadillah, S.K., Basri, H., Ismail, A.F., Othman, M.H.D., Shohur, M.F., and Yunus, M.Z., 2016, Antifouling polysulfone membranes blended with green SiO<sub>2</sub> from rice husk ash (RHA) for humic acid separation, *Chem. Eng. Res. Des.*, 114, 268–279.
- [13] Arthanareeswaran, G., and Starov, V., 2011, Effect of solvents on performance of polyethersulfone ultrafiltration membranes: Investigation of metal ion separations, *Desalination*, 267 (1), 57–63.
- [14] Harun, Z., Jamalludin, M.R., Basri, H., Shohur, M.F., Rosman, N., and Yunus, M.Z., 2013, The effect of synthetic silica on ultrafiltration PSF membrane, *J. Teknol.*, 65 (4), 121–125.
- [15] Shaari, N.Z.K., Sulaiman, N.A., and Abd Rahman, N., 2019, Thin film composite membranes: Preparation, characterization, and application towards copper ion removal, *J. Environ. Chem. Eng.*, 7 (1), 102845.
- [16] Shaari, N.Z.K., Abd Rahman, N., and Mohd Tajuddin, R., 2012, Thin film composite membrane with hybrid membrane as the barrier layer:



- Preparation and characterization, 2012 *IEEE Colloquium on Humanities, Science and Engineering (CHUSER)*, Kinabalu, Malaysia, 3-4 December 2012, 615–620.
- [17] de Lima, S.P.B., de Vasconcelos, R.P., Paiva, O.A., Cordeiro, G.C., de Moraes Chaves, M.R., Filho, R.D.T., de Moraes Rego Fairbairn, E., 2011, Production of silica gel from residual rice husk ash, *Quim. Nova*, 34 (1), 71–75.
- [18] Chik, N.S.I., Shaari, N.Z.K., Ramlee, N.A., and Abdul Manaf, M.R., 2022, Extraction of silica from rice husk ash and its effect on the properties of the integral membrane, *ASM Sci. J.*, 17, 1–13.
- [19] Setyawan, N., Hoerudin, H., and Wulanawati, A., 2019, Simple extraction of silica nanoparticles from rice husk using technical grade solvent: Effect of volume and concentration, *IOP Conf. Ser.: Earth Environ. Sci.*, 309, 012032.
- [20] Sulaiman, N.A., Shaari, N.Z.K., and Abdul Rahman, N., 2016, Removal of Cu(II) and Fe(II) ions through thin film composite (TFC) with hybrid membrane, *J. Eng. Sci. Technol.*, 11, 36–49.
- [21] Chik, N.S.I., and Shaari, N.Z.K., 2022, Effect of rice husk ash gel on the properties of integral membrane from a blend of polysulfone/chitosan/polyvinyl alcohol, *AIP Conf. Proc.*, 2610, 020010.
- [22] Ahmad, A.L., Yusuf, N.M., and Ooi, B.S., 2012, Preparation and modification of poly (vinyl) alcohol membrane: Effect of crosslinking time towards its morphology, *Desalination*, 287, 35–40.
- [23] Geetha, D., Ananthiand, A., and Ramesh, P.S., 2016, Preparation and characterization of silica material from rice husk ash – An economically viable method, *Res. Rev.: J. Pure Appl. Phys.*, 4 (3), 20–26.
- [24] Patel, K.G., Misra, N.M., and Shettigar, R.R., 2016, Preparation and characterization of silica gel from wheat straw, *Int. J. Chem. Eng. Appl.*, 7 (5), 344–347.
- [25] Ravi, S., and Selvaraj, M., 2014, Incessant formation of chain-like mesoporous silica with a superior binding capacity for mercury, *Dalton Trans.*, 43 (14), 5299–5308.
- [26] Alias, S.S., Harun, Z., Manoh, N., and Jamalludin, M.R., 2020, Effects of temperature on rice husk silica ash additive for fouling mitigation by polysulfone–RHS ash mixed-matrix composite membranes, *Polym. Bull.*, 77 (8), 4043–4075.
- [27] Nandiyanto, A.B.D., Oktiani, R., and Ragadhita, R., 2019, How to read and interpret FTIR spectroscopy of organic material, *Indones. J. Sci. Technol.*, 4 (1), 97–118.
- [28] Reyes-Ortega, F., Parra-Ruiz, F.J., Averick, S., Rodríguez, G., Aguilar, M.R., Matyjaszewski, K., and San Román, J., 2013, Smart heparin-based bioconjugates synthesized by a combination of ATRP and click chemistry, *Polym. Chem.*, 4 (9), 2800–2814.
- [29] Ruan, D.S., Li, Y.L., Wang, L., Su, D., and Hou, F., 2010, Fabrication of silicon oxycarbide fibers from alkoxide solutions along the sol–gel process, *J. Sol-Gel Sci. Technol.*, 56 (2), 184–190.
- [30] Tian, S., Ren, W., Li, G., Yang, R., and Wang, T., 2017, A theoretical analysis of pore size distribution effects on shale apparent permeability, *Geofluids*, 2017, 7492328.
- [31] Reino Olegário da Silva, D.A., Bosmuler Zuge, L.C., and de Paula Scheer, A., 2020, Preparation and characterization of a novel green silica/PVA membrane for water desalination by pervaporation, *Sep. Purif. Technol.*, 247, 116852.
- [32] Xu, H.P., Yu, Y.H., Lang, W.Z., Yan, X., and Guo, Y.J., 2015, Hydrophilic modification of polyvinyl chloride hollow fiber membranes by silica with a weak *in situ* sol–gel method, *RSC Adv.*, 5 (18), 13733–13742.