A study on membrane technology for surface water treatment: Synthesis, characterization and performance test

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Abstract. The use of membrane as an innovative technology for water treatment process has now widely been accepted and adopted to replace the conventional water treatment process in increasing fresh water production for various domestic and industrial purposes. In this study, ultrafiltration (UF) membranes with different formulation were fabricated via phase inversion method. The membranes were fabricated by varying the polymer concentration (16 wt%, 18 wt%, 20 wt%, and 21 wt%). A series of tests, such as field emission scanning electron microscope (FESEM), pore size and porosity, contact angle, and zeta potential were performed to characterize the membranes. The membrane performance in terms of permeation flux and rejection were evaluated using a laboratory bench-scale test unit with mine water, lake water and tube well as model feed solution. Long hour filtration study of the membranes provides the information on its fouling property. Few pore blocking mechanism models were proposed to examine the behaviour of flux reduction and to estimate the fouling parameters based on different degree of fouling. 21 wt% PVDF membrane with smaller membrane pore size showed an excellent performance for surface water treatment in which the treated water complied with NWQS class II standard.

Keywords: membrane; water treatment; surface water; lake water; mine water; tube well; water; recycle and reuse

1. Introduction

Water scarcity is a wide definition of water-related issues such as water stress, water shortages, and a prevailing water crisis. Despite the world being covered by more than 70% of water, only 2% of it is fresh and drinkable (with only 1% being easily accessible). This is an alarming rate and is not an ideal amount of water to supply to a global demand of 6.8 billion people (National Geographic 2016). As global warming takes its toll on the human population, several countries even face droughts which can only last up to months due to their geographical location.

Water shortage affects almost all aspects of day-to-day life from regular consumption, agriculture, education, and in some worse cases it is even the cause of death. According to United Nations, 6 to 8 million peoples die annually from the consequences of disasters and water-related diseases (UN Water Cooperation 2013). These negative health-related factors due to water scarcity include (although not limited to) dehydration, exposure to pathogenic microbes, diarrhoea schistosomiasis, trachoma, and intestinal helminths (Tarrass and Benjelloun 2012).

Membrane technology has become more and more popular in water industry because the membrane filtration process can disinfect water without chemical addition and avoid the formation of toxic disinfection by-products. The use of membrane as an innovative technology for water treatment process has now widely been accepted and adopted to replace the conventional water treatment process in increasing fresh water production for various domestic and industrial purposes (Rojas-Serrano *et al.* 2015). With its advantages such as small operation area, high filtration efficiency as well as direct operational handling, membrane had emerged as a favorable filter media for water treatment system.

With the current critical water shortage problems in the world, this study is aimed to cope this problem by looking into the potential of treating lake water, mine water, and tube well water for reclamation and reuse. Since membrane technology has been widely applied worldwide in treating various types of water and wastewater, therefore it has great potential to be utilized for water reuse programmes. The objectives of this study are (1) to fabricate and characterize polymeric membranes with different formulation, (2) to investigate the efficiency of polymeric membrane with different structural properties for mine water, lake water and tube well water reuse, and (3) to analyse the fouling mechanism of each polymeric membrane for long hour filtration process.

2. Materials and methods

2.1 Materials

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Table 1 Membrane polymer solution formulation

Membrane Number	PVDF (wt.%)	DMAc (wt.%)
M1	16	84
M2	18	82
M3	20	80
M4	21	79

Polyvinylidene fluoride (PVDF) powder (TA6010/1001) purchased from Solvay Solexis, Shanghaiwas used as the membrane polymer. Whereas, N,N-dimethylacetamide (DMAc) (purity (GC)≥99%) purchased from Merck, Germany was used as the solvent to dissolve the polymer.

2.2 Sample collection points

Lake water used in this study was collected from Tasik Putrajaya located at Putrajaya, Malaysia (2.902481, 101.671449). Mine water used in this study was collected from Tasik Bandar Saujana Putra, located at Jenjarom, Selangor, Malaysia (2.942723, 101.571640). Tube well water in this study was collected from tube well at Kolej Keris Mas, Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor, Malaysia (2.926981, 101.788484).

2.3 Membrane synthesis

Flat sheet membranes were synthesized from different polymer solution formulation via phase inversion method as summarized in Table 1. First, pre-weighted PVDF powder and DMAc solvent were placed in a beaker. The mixture was then employed to a stirring rate of 250 rpm at 65°C for 4 hours on a hotplate to obtain a complete dissolution of polymer solution. The temperature was then reduced to 40°C and the solution was stirred for another 4 hours. The polymer solution was then left overnight. During the casting process, polymer solution was poured evenly into a solution chamber. The casting process was then started. The casted nascent membrane on the glass plate was removed from the platform and immersed gently into the coagulation bath immediately. The immersion was left for a day to ensure complete solidification and removal of residual solvent from the membrane (Damodar *et al.* 2009).

2.4 Membrane characterization

2.4.1 Field emission scanning electron microscope (FESEM)

FESEM (Zeiss Supra-55VP, Germany) was used to observe the top and cross-section surface morphology of the synthesized membranes. Membrane samples were sputtered with a thin layer of platinum prior FESEM analysis to provide electrical conductivity and to prevent membrane surface from being charged up (Yunos *et al.* 2014). All membrane samples in this study were examined at potential of 15 kV and 5 kV for surface and cross-section observation, respectively.

2.4.2 Porosity and pore size

Porosity of the membrane was determined by gravimetric method using Eq. (1) (Rezaee *et al.* 2015). First, the membrane was cut into 4 small pieces (1 cm×1 cm) and immersed in distilled water at 25°C for 24 hours. Then, the membrane surface was dried with a filter paper and the average weight of the wet membrane (W_w) was recorded using an electronic weight balance. The wet membrane was then dried in an oven for 24 hours at 50°C and the average weight of the dried membrane (W_d) was recorded.

$$\varepsilon = \frac{\frac{W_w - W_d}{\rho_w}}{\frac{W_w - W_d}{\rho_w} + \frac{W_d}{\rho_m}} \tag{1}$$

where ε is the porosity of the membrane, W_w is the weight of wet membrane (g), W_d is the weight of dried membrane (g), ρ_w is the density of distilled water (0.998 g/mL), and ρ_m is the density of PVDF (1.74 g/mL at 25°C). Membrane pore size was then determined using the Guerout-Elford-Ferry equation (Basri *et al.* 2011)

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \tag{2}$$

where r_m is the mean pore radius (m), η is the water viscosity (8.9×10^{-4} Pa s), l is the membrane thickness (m), Q is the volume of permeate water per-unit time (m³/s), A is the membrane area (m²), and ΔP is the operational pressure (Pa).

2.4.3 Contact angle

The wettability of membrane surface was measured by contact angle using the sessile drop technique using easy drop device DSA100 (Kruss GmbH, Germany). The contact angle measurement was taken at five different locations on the membrane surface for each membrane sample to minimize the analytical error.

2.4.4 Streaming potential

The surface charge of membrane was assessed by zeta potential measurement using Malvern Zeta Sizer Nano ZS (Malvern Instruments, UK) at field strength of 25 V/cm. Universal dip cell is used where the measurement routine is the same as that for the folded capillary cell for suspended particles zeta potential measurement except that the fast field reversal (FFR) measurement is not used. The measurement electrodes on the dip cell are only 2 mm apart and positioned right next to the measurement zone. This removes the effect of electroosmosis and therefore the need for the FFR part of the measurement routine.

2.5 Membrane performance evaluation

A laboratory bench-scale dead-end test rig was used to study performance of the fabricated membrane in terms of permeation flux and rejection. For permeate flux measurement, membrane was first compacted at 3 bar with ultra-pure water for 30 min until a constant permeate flux was obtained. Followed by compaction, the membrane was then subjected to different pressure of 1.0, 1.5, 2.0, and 3.0 bar to determine the respective permeate flux. Permeate flux (F) was determined by direct measurement of the

Table 2 Fouling mechanisms with their corresponding model equation (Wang *et al.* 2012)

Fouling mechanism	Equation	n
Complete pore blocking	$\ln\left(\frac{1}{J}\right) = \ln\left(\frac{1}{J_o}\right) + k_1 t$	2
Pore constriction	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_o}} + k_2 t$	1.5
Intermediate pore blocking	$\frac{1}{J} = \frac{1}{J_o} + k_3 t$	1
Cake filtration	$\frac{1}{J^2} = \frac{1}{J_o^2} + k_4 t$	0

permeate volume over the time using Eq. (3) (Teow *et al.* 2012).

$$F = \frac{V}{At} \tag{3}$$

where F is the permeate flux (L/m^2 h), V is the permeate volume (L), A is the effective membrane area (0.00146 m^2), and t is the time (h). Membrane rejection (R (%)) was calculated from the concentration of feed solution and permeate solution using the following equation

$$R(\%) = \left(1 - \frac{Cp}{Cf}\right) \times 100\% \tag{4}$$

where R is the rejection (%), C_p is the concentration of the permeate solution (mg/L), and C_f is the concentration of the feed solution (mg/L).

2.6 Membrane fouling study

During the membrane fouling study, the membrane was subjected to constant pressure of 1.5 bar for two hours and the flux was recorded for every minute. Membrane fouling mechanism was determined using four different fouling model summarized in Table 2 (Wang *et al.* 2012).

2.7 Water sample analysis

pH of the water sample was determined using a pH meter (Hanna Instruments Inc., USA). TDS was measured using a TDS meter probe (Hanna Instruments Inc., USA). Turbidity in water sample was determined using a Hach DR/2000 direct reading spectrophotometer (Hach, USA). Colour, TSS, COD, and NH$_3$-N of the water sample were measured using a HACH DR3900 spectrophotometer med RFID-technology (Hach, USA). Heavy metals were analysed using Flame Atomic Absorption Spectroscopy (AAS) (Aligent Technologies Inc., USA).

3. Results and discussion

3.1 Membrane characterization

3.1.1 Membrane morphology

Figs. 1(a) and 1(b) show the FESEM images of the surface and cross-sectional of fabricated membranes at different PVDF weight percent (16 wt%, 18 wt%, 20 wt%, and 21 wt%). From Fig. 1(a), it can be observed that all fabricated membranes were having porous surface morphology regardless of the PVDF weight percent used in
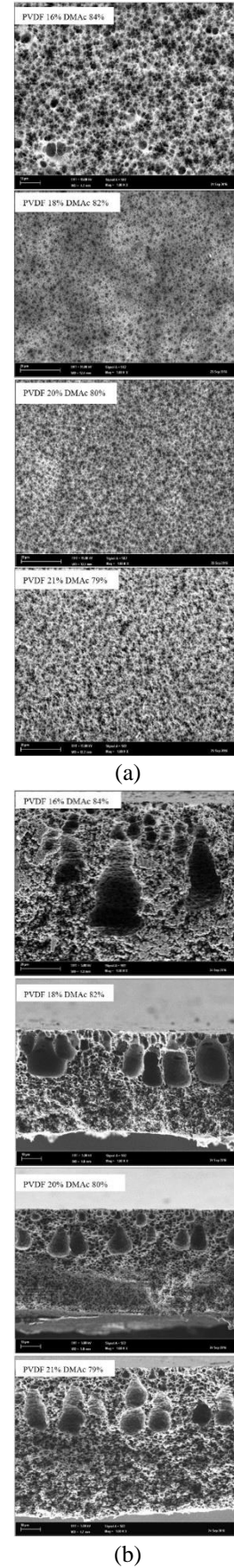

(a)

(b)

Fig. 1 FESEM images of the (a) surface morphology and (b) cross-section of fabricated membranes at the magnification of 1.0 k×
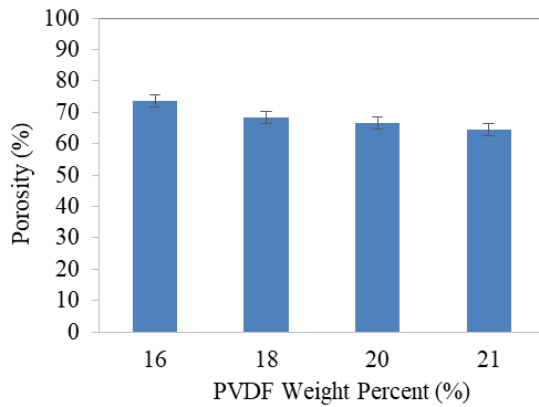
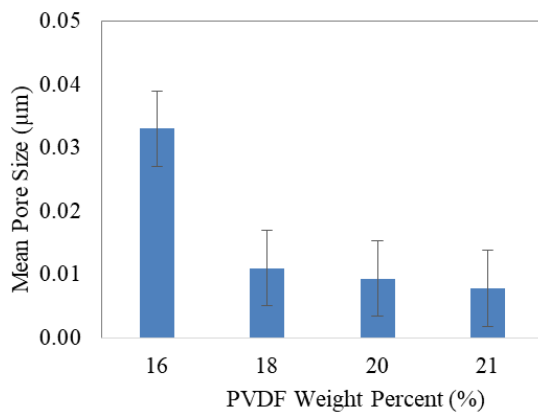Fig. 2 Membrane porosity of the fabricated membranes at different PVDF weight percent

Fig. 4 Contact angle of the fabricated membranes at different PVDF weight percent

Fig. 3 Membrane mean pore size of the fabricated membranes at different PVDF weight percent

0.033 μm to 0.0078 µm when the PVDF weight percent was increased from 16 wt% to 21 wt%. As the PVDF weight percent was increased, membrane polymer solution viscosity increased. Thus the exchange rate between solvent and non-solvent in the coagulation bath was decreased which results in smaller membrane pores and lower membrane porosity (Bakeri *et al.* 2010). This phenomenon was also supported by FESEM images of the fabricated membranes depicted in Fig. 1(a). Similar results were obtained by Bakeri *et al.* (2010) and Yeow *et al.* (2004) whereby the membrane porosity was decreased with the increasing of polyetherimide (PEI) and PVDF concentration, respectively. In addition, Susan *et al.* (2016) observed that the membrane pore size was reduced as the PVDF concentration was increased in membrane polymer solution. In a nutshell, the higher the polymer weight percent, the lower the membrane porosity and membrane pore size.

3.1.3 Contact angle

As illustrated in Fig. 4, it can be seen that the contact angle of the fabricated membranes was increased proportionally to the PVDF weight percent in which the membrane contact angle was increased from 77.54±0.29˚ to 81.7±0.42˚ as the PVDF weight percent was increased from 16 wt% to 21 wt%. This means that the membrane had adapted to a more hydrophobic nature. According to Rana and Matsuura (2010), membrane material, surface porosity, and surface roughness have an important influence on membrane wettability. With the increasing of PVDF weight percent, the fabricated membrane was adapted with a more hydrophobic nature due to the addition of hydrophobicity PVDF. Therefore, without any surprise, the contact angle was increased with the increasing of PVDF weight percent.

3.1.4 Zeta potential

Fig. 5 shows the zeta potential of the fabricated membranes at different PVDF weight percent. The zeta potential value of the fabricated membrane was decreased with the increasing of PVDF weight percent. However, the increment of zeta potential value was not significant. It was postulated that the change of surface zeta potential was not significant as the membranes were fabricated from the same material (PVDF).

membrane polymer formulation. As the PVDF weight percent was increased, the membrane pore size was reduced. Similar results have been obtained by Susan *et al.* (2016). On the other hand, the cross-section FESEM images in Fig. 1(b) shows that all fabricated membranes exhibited fingerlike and macrovoid structure. As the PVDF weight percent was increased, the length of fingerlike structure and the cavity of macrovoid decreased correspondlingly. According to Kuilla *et al.* (2010) and Li *et al.* (2012), the morphology of the fabricated membrane is directly related to the exchange rate of solvent and non-solvent in the coagulation bath. Higher PVDF weight percent will produce membrane polymer solution with higher viscosity (Rezaee *et al.* 2015). Higher polymer solution viscosity is then contributed to slower solvent (DMAc) and non-solvent (water from coagulation bath) exchange rate due to higher diffusion resistance for polymer aggregation (Yuliwati and Ismail 2011). Hence, resulted in smaller pores, spongy or less void structure.

3.1.2 Porosity and pore size

Figs. 2 and 3 show the membrane porosity and pore size of the fabricated membranes at different PVDF weight percent, respectively. As clearly seen from the figures, the porosity and pore size of the membrane was decreased with the increasing of PVDF weight percent in polymer solution. The porosity of the membrane was reduced from 73.5% to 64.5%, whereas the membrane pore size was reduced from
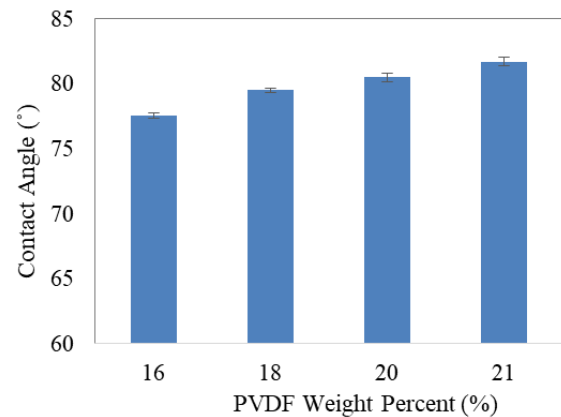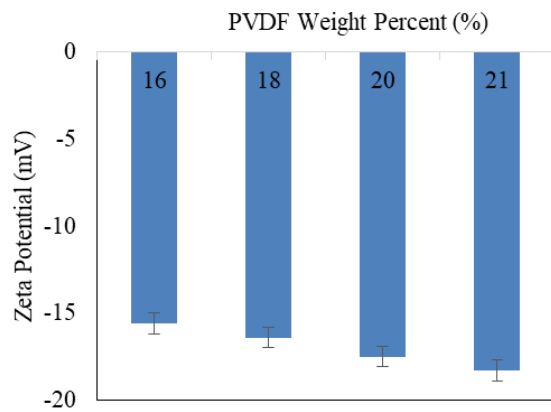
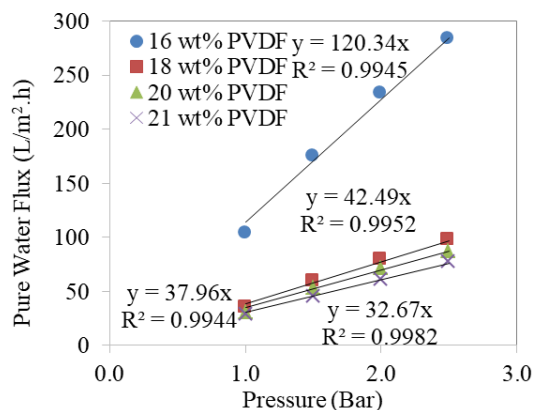Fig. 5 Zeta potential of the fabricated membranes at different PVDF weight percent (0.1 mM NaCl at pH 7)

Fig. 6 Membrane permeability for the fabricated membranes at different PVDF weight percent

Table 3 Permeate flux of the membranes in treating lake water, mine water and tube well water

PVDF Weight Percent (wt%)	Permeate Flux (L/m² h bar)		
	Lake Water	Mine Water	Tube Well Water
16	89.59	88.76	88.01
18	51.54	53.42	52.19
20	50.55	50.42	50.54
21	44.56	44.38	45.21

3.2 Membrane performance evaluation

3.2.1 Membrane permeability

Fig. 6 shows the permeability of the fabricated membranes at different PVDF weight percent. It can be seen from the figure that the pure water flux for all membranes was increased linearly with the increasing of applied pressure. The permeability of each membrane was defined as the slope of pure water flux versus applied pressure in which the permeability for membrane fabricated at 16 wt%, 18 wt%, 20 wt%, and 21 wt% of PVDF was 120.34 L/m² h bar, 42.49 L/m² h bar, 37.96 L/m² h bar, and 32.67 L/m² h bar, respectively. The membrane permeability was reduced as the PVDF weight percent was increased. Theoretically, membrane permeability is dependent on various membrane properties such as porosity, pore size, and hydrophilicity (Lalia *et al.* 2013). As the PVDF weight

percent in the membrane polymer solution was increased from 16 wt % to 21 wt %, the resulted membrane's contact angle was increased; whereas the porosity and pore size were decreased proportionally. Higher contact angle value for the membrane with higher PVDF weight percent means that the respective membrane was having lower wettability as discussed in previously. In addition, less porous and smaller pore size of the membrane with higher PVDF weight percent also attributed to the lower membrane permeability (Liu *et al.* 2016).

3.2.2 Permeation flux and rejection

The permeate flux of the fabricated membranes in treating lake water, mine water, and tube well water are listed in Table 3. As depicted in Table 3, permeate flux of the membrane was decreased as the PVDF weigh percent of the fabricated membrane was increased from 16 wt% to 21 wt% regardless of the type of feed solution used in membrane treatment. This is because as the PVDF weight percent of the membrane was increased, membrane pore size and porosity were decreased, whereas an increase in contact angle was observed. Hence, with more hydrophobic surface and less penetration area, membrane with higher PVDF weight percent was deserving for lower permeate flux (Leo *et al.* 2016).

On the other hand, Tables 4-6 show the raw water and permeate water quality of lake water, mine water, and tube well water, respectively after being treated with membrane at different PVDF weight percent. In general, the lake water was having the best quality among all feed solution samples by presenting lower value in several parameters such as conductivity, TDS, colour, turbidity, NH_3-N, and Zn. However, improvement in water quality could be observed for in all water samples after being treated with membranes. Membrane with 21 wt% of PVDF shows excellent performance for surface water treatment in which the conductivity, TDS, colour, turbidity, TSS, NH_3-N, COD, Cr, Cu, Cd, Pb, Zn, Ni, and Na were reduced 35.41-41.45%, 41.23-42.74%, 89.72-95.04%, 84.64-87.68%, 89.50-91.00%, 85-87.20%, 80.08-85.81%, 70-88.19%, 92.00-94.76%, 57.76-69.38%, 64.14-71.85%, 76.00-82.28%, 73.62-75.54%, and 19.04-20.98%, respectively. It is not a surprise that membrane with 21 wt% of PVDF was showing the highest rejection for all parameters. This is because 21 wt% PVDF membrane was having the smallest membrane pore size as compared to other membranes in this study. Therefore, it has greater capability to reject large amount of solute which has larger particle size than the membrane pore size.

Table 4 Raw and permeate water quality of lake water after being treated with membrane at different PVDF weight percent

Parameter	Unit	Raw water sample	Permeate Water Treated with Membrane of Different PVDF Weight Percent (wt%)				DWQS[a]	NWQS[b]					
			16 wt%	18 wt%	20 wt%	21 wt%		I	IIA	IIB	III	IV	V
pH		7.96	6.92	7.24	7.32	7.14	6.5-9.0	6.5-8.5	6.5-9.0	6.5-9.0	5-9	5-9	-
Conductivity	µs	137.40	121.20	102.60	85.96	80.45	250	1000	1000	-	-	6000	-
TDS	ppm	68.90	59.50	51.20	42.34	40.24	1000	500	1000	-	-	4000	-

Table 4 Continued

Parameter	Unit	Raw water sample	Permeate Water Treated with Membrane of Different PVDF Weight Percent (wt%)				DWQS[a]	NWQS[b]					
			16 wt%	18 wt%	20 wt%	21 wt%		I	IIA	IIB	III	IV	V
Colour	PtCo	53.00	44.00	24.00	10.52	5.45	15	15	150	150	-	-	-
Turbidity	NTU	25.20	15.60	10.50	5.82	3.87	5	5	50	50	-	-	-
TSS	mg/L	12.00	8.00	4.00	3.00	1.12	−	25	50				
NH$_3$-N	mg/L	0.12	0.09	0.05	0.02	0.02	1.5	0.1	0.3	0.3	0.9	2.7	>2.7
COD	mg/L	26.00	18.54	12.24	5.42	4.12	-	10	25	25	50	100	>100
Cr	mg/L	0.13	0.09	0.06	0.02	0.02	0.05	<0.05	0.05	0.05	0.07	0.1	>0.1
Cu	mg/L	0.02	0.01	0.01	0.00	0.00	1	<0.02	0.02	0.02	-	-	>0.02
Cd	mg/L	13.52	10.54	8.12	6.24	4.14	0.003	<0.01	0.01	0.01	-	-	>0.01
Pb	mg/L	0.93	0.75	0.54	0.34	0.28	0.01	-	-	-	-	-	-
Zn	mg/L	0.04	0.03	0.02	0.01	0.01	3	<5	5	5	0.4	2	>2
Ni	mg/L	0.14	0.13	0.10	0.05	0.03	0.02	<0.05	0.05	0.05	-	0.2	>0.2
Na	mg/L	5.09	4.78	4.76	4.32	4.12	200	-	-	-	-	-	-

[a]Drinking Water Quality Standard (DWQS), Ministry of Health, Malaysia
[b]National Water Quality Standard (NWQS), Ministry of Environment, Malaysia

Table 5 Raw and permeate water quality of mine water after being treated with membrane at different PVDF weight percent

Parameter	Unit	Raw Water Sample	Permeate Water Treated with Membrane of Different PVDF Weight Percent (wt%)				DWQS[a]	NWQS[b]					
			16 wt%	18 wt%	20 wt%	21 wt%		I	IIA	IIB	III	IV	V
pH		4.57	5.84	5.40	4.89	4.86	6.5-9.0	6.5-8.5	6.5-9.0	6.5-9.0	5-9	5-9	-
Conductivity	µs	186.50	168.74	144.25	122.34	114.26	250	1000	1000	-	-	6000	-
TDS	ppm	93.40	80.59	68.95	60.44	53.48	1000	500	1000	-	-	4000	-
Colour	PtCo	65.28	53.85	22.46	6.54	3.24	15	15	150	150	-	-	-
Turbidity	NTU	26.30	18.55	13.57	5.42	3.24	5	5	50	50	-	-	-
TSS	mg/L	6.00	4.12	2.14	1.58	0.54	−	25	50				
NH$_3$-N	mg/L	0.25	0.18	0.12	0.05	0.03	1.5	0.1	0.3	0.3	0.9	2.7	>2.7
COD	mg/L	7.40	5.12	3.45	2.14	1.05	-	10	25	25	50	100	>100
Cr	mg/L	0.04	0.03	0.02	0.01	0.01	0.05	<0.05	0.05	0.05	0.07	0.1	>0.1
Cu	mg/L	0.12	0.08	0.05	0.04	0.01	1	<0.02	0.02	0.02	-	-	>0.02
Cd	mg/L	13.49	10.54	8.24	6.78	4.21	0.003	<0.01	0.01	0.01	-	-	>0.01
Pb	mg/L	1.03	0.82	0.55	0.33	0.29	0.01	-	-	-	-	-	-
Zn	mg/L	0.33	0.24	0.18	0.12	0.06	3	<5	5	5	0.4	2	>2
Ni	mg/L	0.31	0.26	0.20	0.13	0.08	0.02	<0.05	0.05	0.05	-	0.2	>0.2
Na	mg/L	3.54	3.24	3.21	3.04	2.80	200	-	-	-	-	-	-

[a]Drinking Water Quality Standard (DWQS), Ministry of Health, Malaysia
[b]National Water Quality Standard (NWQS), Ministry of Environment, Malaysia

The permeate water obtained after the membrane filtration processes were than compared with Drinking Water Quality Standards (DWQS) and National Water Quality Standards (NWQS) of Malaysia. DWQS is a

Table 6 Raw and permeate water quality of tube well water after being treated with membrane at different PVDF weight percent

Parameter	Unit	Raw water sample	Permeate water treated with membrane of different PVDF weight percent (wt%)				DWQS[a]	NWQS[b]					
			16 wt%	18 wt%	20 wt%	21 wt%		I	IIA	IIB	III	IV	V
pH		6.65	6.92	7.15	7.23	7.18	6.5-9.0	6.5-8.5	6.5-9.0	6.5-9.0	5-9	5-9	-
Conductivity	µs	290.20	265.56	230.24	210.54	187.45	250	1000	1000	-	-	6000	-
TDS	ppm	145.00	130.52	110.63	95.41	85.21	1000	500	1000	-	-	4000	-
Colour	PtCo	83.00	69.00	27.00	12.00	8.00	15	15	150	150	-	-	-
Turbidity	NTU	29.60	21.80	13.40	4.78	3.74	5	5	50	50	-	-	-
TSS	mg/L	14.00	10.00	8.00	3.00	1.47	−	25	50				
NH$_3$-N	mg/L	0.45	0.32	0.21	0.10	0.07	1.5	0.1	0.3	0.3	0.9	2.7	>2.7
COD	mg/L	12.40	8.54	6.24	3.24	2.47	-	10	25	25	50	100	>100
Cr	mg/L	0.00	0.00	0.00	0.00	0.00	0.05	<0.05	0.05	0.05	0.07	0.1	>0.1
Cu	mg/L	0.00	0.00	0.00	0.000	0.00	1	<0.02	0.02	0.02	-	-	>0.02
Cd	mg/L	24.24	18.99	17.32	12.33	10.24	0.003	<0.01	0.01	0.01	-	-	>0.01
Pb	mg/L	0.24	0.18	0.15	0.10	0.09	0.01	-	-	-	-	-	-
Zn	mg/L	0.05	0.04	0.03	0.02	0.01	3	<5	5	5	0.4	2	>2
Ni	mg/L	0.00	0.00	0.00	0.00	0.00	0.02	<0.05	0.05	0.05	-	0.2	>0.2
Na	mg/L	11.47	10.98	10.58	9.85	9.21	200	-	-	-	-	-	-

[a]Drinking Water Quality Standard (DWQS), Ministry of Health, Malaysia
[b]National Water Quality Standard (NWQS), Ministry of Environment, Malaysia

standard set by Ministry of Health Malaysia on maximum permissible limit of various parameters for drinking water. Whereas, NWQS are standards set by Ministry of Environment Malaysia for water with different usage. NWQS can be classified into five major classes: class I water can be used for conservation of natural environment and for very sensitive aquatic species, class IIA water can be used for sensitive aquatic species, class IIB water can be used for recreational usage with body contact, class III water can be used for livestock drinking and other tolerant species, class IV water can be used for irrigation, and class V water can be used for miscellaneous usage other than mentioned in class I-IV.

Although membrane filtration process had improved the treated water quality to a certain extent, it was still not able to meet DWQS as several heavy metals concentrations are still high. The aforementioned heavy metals include Cd, Pb, and Ni. However, most of the samples after the membrane filtration were able to meet NWQS class III quality in which these treated water could be used for livestock drinking and other tolerant species, except 16 wt% PVDF membrane used in treating lake water. With lower permeate water quality, lake water treated with 16 wt% PVDF membrane was categorized in NWQS class IV whereby it can be used for irrigation.

3.3 Fouling study

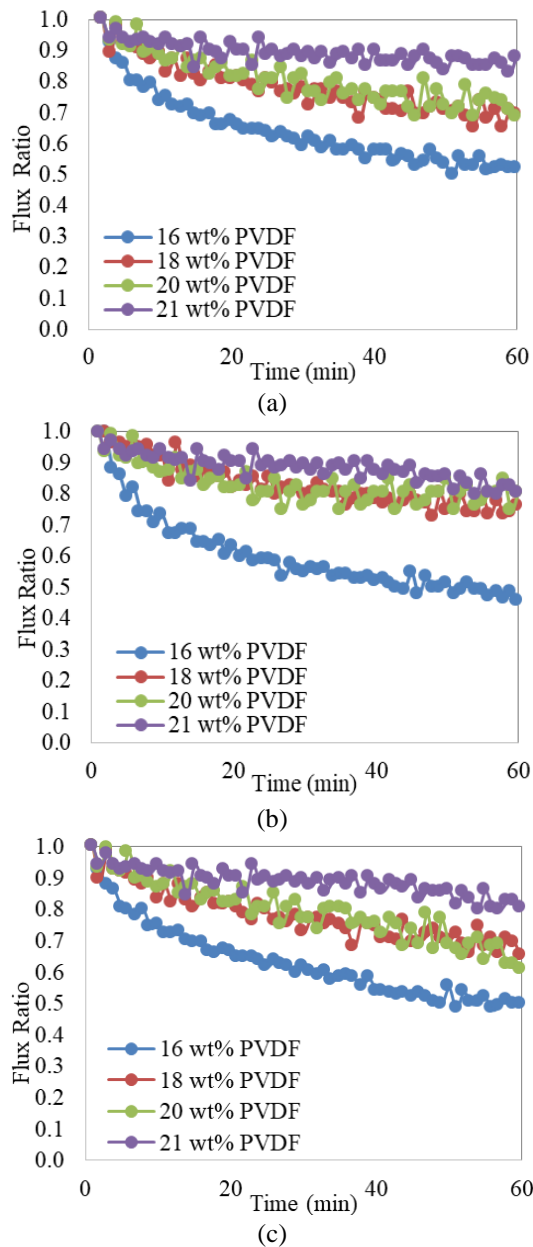Fig. 7 shows the flux ratio of the fabricated membranes

Fig. 7 Flux ratio of the fabricated membranes at different PVDF weight percent in treating (a) lake water (b) mine water and (c) tube well water (operating pressure = 1.5 bar)

Table 7 Values of k and correlation coefficient (R^2) based on various blocking mechanism model equations for flux reduction at 1.5 bar in lake water filtration

PVDF wt%	n = 0		n = 1		n = 1.5		n = 2	
	k_4	R^2	k_3	R^2	k_2	R^2	k_1	R^2
16	6.3×10^{-6}	0.9099	2.0×10^{-4}	0.8069	8.2×10^{-4}	0.7194	0.0135	0.6022
18	5.4×10^{-6}	0.8162	3.1×10^{-4}	0.7532	5.7×10^{-4}	0.7471	0.0062	0.7132
20	13×10^{-6}	0.7362	4.8×10^{-4}	0.7281	9.7×10^{-4}	0.7199	0.0075	0.7088
21	69×10^{-6}	0.8317	2.7×10^{-4}	0.8071	5.7×10^{-4}	0.7814	0.0059	0.7414

Table 8 Values of k and correlation coefficient (R^2) based on various blocking mechanism model equations for flux reduction at 1.5 bar in mine water treatment

PVDF wt%	n = 0		n = 1		n = 1.5		n = 2	
	k_4	R^2	k_3	R^2	k_2	R^2	k_1	R^2
16	5.6×10^{-6}	0.9110	1.8×10^{-4}	0.8339	7.4×10^{-4}	0.7697	0.0122	0.6854
18	4.8×10^{-6}	0.8179	1.2×10^{-4}	0.7826	4.1×10^{-4}	0.7600	0.0057	0.7340
20	13×10^{-6}	0.7323	2.3×10^{-4}	0.6943	6.8×10^{-4}	0.6656	0.0080	0.6296
21	67×10^{-6}	0.8403	1.3×10^{-4}	0.8129	4.3×10^{-4}	0.7935	0.0055	0.7710

Table 9 Values of k and correlation coefficient (R^2) based on various blocking mechanism model equations for flux reduction at 1.5 bar in tube well water treatment

PVDF wt%	n = 0		n = 1		n = 1.5		n = 2	
	k_4	R^2	k_3	R^2	k_2	R^2	k_1	R^2
16	2.0×10^{-6}	0.9390	7.4×10^{-5}	0.9228	3.2×10^{-4}	0.9091	0.0054	0.8911
18	5.8×10^{-6}	0.8239	25×10^{-5}	0.7231	6.4×10^{-4}	0.7854	0.0043	0.7157
20	15×10^{-6}	0.7526	37×10^{-5}	0.6447	7.1×10^{-4}	0.6425	0.0094	0.6027
21	73×10^{-6}	0.8104	11×10^{-5}	0.8426	6.8×10^{-4}	0.7735	0.0063	0.7421

at different PVDF weight percent in treating lake water, mine water, and tube well water. As depicted in Fig. 7, 16 wt% PVDF membrane showed the most drastic flux decline. Whereas, 18 wt% PVDF membrane and 20 wt% PVDF membrane were having the similar permeate flux profile, which is higher flux ratio than 16 wt% PVDF membrane; while 21 wt% PVDF membrane was experiencing the least membrane fouling. Membranes with higher PVDF weight percent had shown enhancement in membrane fouling phenomenon. This possibly is due to the combination of several membrane properties such as membrane hydrophilicity, pore size, porosity, and zeta potential.

As discussed earlier, the fabricated membrane was adapted with a more hydrophobic nature with the increasing of PVDF weight percent due to the addition of hydrophobicity PVDF. Therefore, more hydrophobic PVDF membrane at higher PVDF weight percent was expected to endure with more severe membrane fouling as most of the solute particles are hydrophobic in nature (Xia and Ni 2014). Surprisingly, our finding was contradicting with the expected result in which membrane with higher hydrophobic nature underwent less membrane fouling. This could be explained by the pore size, porosity, and zeta potential of the membrane which play a more dominant role in affecting membrane fouling phenomenon.

As reported in pore size and porosity characterization, the membrane porosity and pore size were decreased with the increasing of PVDF weight percent. Hence, solute particles which have particle size greater than the membrane pore size will not be able penetrate into the membrane matrix; thus contributed to less membrane fouling. Similar results have been obtained by Susan *et al.* (2016) in which they found that the membrane with highest porosity and pore size had a higher tendency of fouling. Additionally, zeta potential is also an important factor in affecting membrane fouling. 21 wt% PVDF membrane with slightly greater zeta potential value will have greater potential to repel the negative charge solute particle

(Zazouli *et al.* 2010). Therefore, dedicate for less membrane fouling.

3.4 Membrane fouling mechanism

Various blocking mechanism models were used in this study to examine the membrane fouling mechanism, including cake filtration (n=0), intermediate pore blocking (n=1), pore constriction (n=1.5), and complete pore blocking (n=2). Values of k and correlation coefficient (R^2) of each blocking mechanism model were summarized in Tables 7-9.

Results from the blocking mechanism model fitting shows that cake filtration model (n=0) was correlating well with the permeate flux profile of the membranes in this study regardless the type of feed solution. Cake filtration phenomenon is attributed to the fouling mechanism in which the solute particles are much larger than the membrane pore size (Huang *et al.* 2008). Through the cake filtration phenomenon, a uniform solute cake layer will form over the membrane surface thus exerted resistance for fluid flow. In order to conserve the membrane performance for long term operation, periodic physical cleaning through backwashing followed by forward washing and chemical cleaning are recommended.

The positive k value obtained from the cake filtration model designated that membrane pore blocking was due to the cake filtration mechanism that had happened. Lower k value indicated a slower pore blocking rate. As the PVDF weight percent was increased, k value was decreased simultaneously. The k value trending obtained through cake filtration model agreed well with the membrane characteristics and membrane fouling propensity. Membrane with highest PVDF weight percent (21 wt%) was dedicated for less membrane fouling. It correlates well with the lowest k value from cake filtration model as compared to other fabricated membranes.

4. Conclusions

Membranes with different PVDF weight percent (16 wt%, 18 wt%, 20 wt%, and 21 wt%) were successfully fabricated through phase inversion method using PVDF as polymer and DMAc as solvent. Performance test of the fabricated membrane in treating lake water, mine water, and tube well water showed that membrane treatment had improved the water quality of the water samples. Among all fabricated membranes, 21 wt% PVDF membrane with smaller membrane pore size showed an excellent performance for the water treatment in which the conductivity, TDS, colour, turbidity, TSS, NH_3-N, COD, Cr, Cu, Cd, Pb, Zn, Ni, and Na were reduced 35.41-41.45%, 41.23-42.74%, 89.72-95.04%, 84.64-87.68%, 89.50-91.00%, 85-87.20%, 80.08-85.81%, 70-88.19%, 92.00-94.76%, 57.76-69.38%, 64.14-71.85%, 76.00-82.28%, 73.62-75.54%, and 19.04-20.98%, respectively. The permeate water quality treated with 21 wt% PVDF membrane were within the DWQS standards for all parameters except for Cd, Pb, and Ni which were slightly

higher. However, all the parameters were complying well with NWQS for class III and above. Hence, the treated water by 21 wt% PVDF membrane was able to achieve the objective of recycling and reuse in which it could be used for recreational and irrigation purposes. Results from the blocking mechanism model fitting showed that cake filtration model (n=0) correlates well with permeate flux profile of the membranes in this study regardless of the type of feed solution. In conclusion, all findings in this study had contributed to the possibility of developing the membrane technology for Malaysia's surface water treatment for non-potable water reuse.

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