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# Enlargement of oil droplets by using asymmetric structure of polyvinylidene fluoride membranes

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**Abstract.** This paper presents a study for enlarging the oil droplets by using the polyvinylidene fluoride (PVDF) membranes in a cross-flow membrane filtration system at the transmembrane pressures range between 0 and 4 bars. The PVDF membranes are fabricated by using phase inversion technique with different concentrations of coagulant ethanol (0 – 30 v/v%). Alkaline-surfactant-polymer (ASP) produced water is synthesised and tested as the feed solution with the oil droplets sized between 0.1 and 0.2  $\mu\text{m}$ . Results show that the effect of the membrane formulations on the oil droplet coalescence is lesser as compared to the effect of the transmembrane pressures. More than 65% of the coalesced oil droplets in permeate having the diameters exceeding 1.0  $\mu\text{m}$  although at least 50% of the membrane pores are larger than the oil droplets in the feed solutions. It is suggested that the tortuous structure of the membranes coalesced the oil droplets significantly.

## 1. Introduction

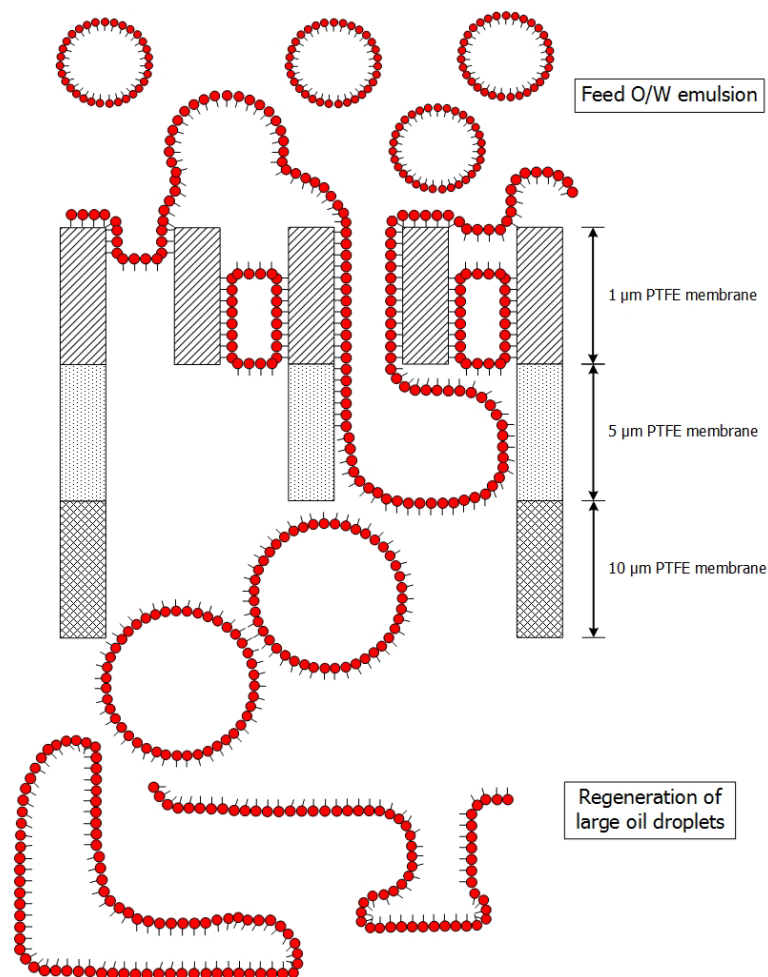
Alkaline-surfactant-polymer (ASP) flooding technology is economically attractive to improve the oil recovery especially from the geologically challenging reservoirs [1]. One of the drawbacks of ASP is the management of the produced water which containing the tough emulsions due to the combination of the chemicals [2 – 5]. The conventional treatment systems in the existing oilfields include cyclones, floatation tanks, settling tanks and coalescers [6 – 7]. However, these treatment systems are mostly designed for water and polymer flooding produced water, and may not meet the requirement for the produced water from the ASP flooding [8]. Application of demulsifiers are thus developed to treat the ASP produced water [8 – 9]; but the excess demulsifiers will create a secondary wastewater. Although the ASP has been developed since three decades ago [10], the research on the more sustainable treatment systems on ASP produced water is still limited.

Membrane separation technology is proposed to be the best option to treat the produced water from ASP flooding. The advantages of the membrane separation technology in this application include [11 – 12]: (1) no addition of chemical demulsifiers is required; thus, no secondary wastewater can be produced; (2) the requirement of the mechanical parts for the membrane systems is less; hence, the flowsheet of the membrane systems is simple and the footprint of the membrane systems is small; these make the membrane systems become more preferable for offshore application because the space and weight in the offshore production deck are limited; (3) a minimal maintenance; and (4) easy start-up and shut-down.



Lately, membrane separation technology has been attractive in oily wastewater treatment [13]. The targeted oils such as petroleum oils, vegetable oils and cutting oils [14 – 16] as well as other pollutants are rejected by hydrophilic membranes; while the clean water is recovered as permeate. Because the ASP produced water contains various chemicals, recovery of the crude oil as the permeate by using hydrophobic and oleophilic membranes are considered. However, the information on recovering the oil from ASP produced water using membrane separation is scarcely reported.

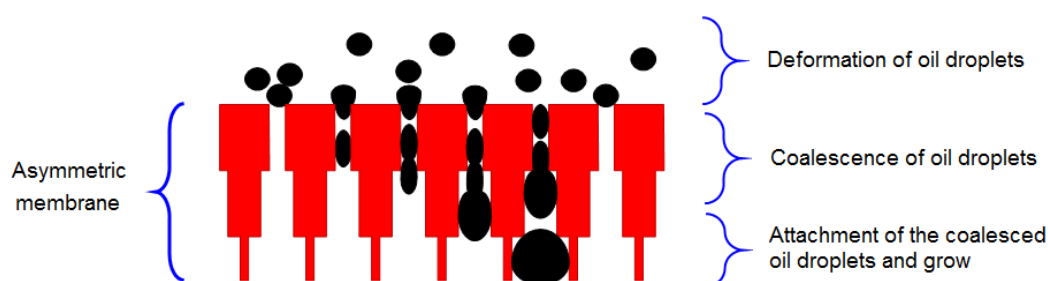
Various commercial hydrophobic membranes have been examined for coalescing the oil droplets [17 – 18]. The oil droplet sizes as well as the oil separation rates increase with the polytetrafluorethylene (PTFE) membrane pore sizes of 0.2 – 10  $\mu\text{m}$  [19 – 21]. The polypropylene (PP) membrane with the effective pore size of 0.05  $\mu\text{m}$  has no essential influence on the coalescence of the oil droplets [22]. Kawakatsu et al. [23] revealed that the oil fraction and the amount of the oil in the permeate increased when three PTFE membranes with different pore sizes i.e. 1, 5 and 10  $\mu\text{m}$  were stacked into one layer. The membrane with pore size of 1  $\mu\text{m}$  is able to breakdown the emulsion when the feed solution is pressured and permeated through the membrane; while the membranes with pore sizes of 5 and 10  $\mu\text{m}$  provide the space for the coalesced oil droplets to grow, as shown in Figure 1. Although the oil recovery performance is better when using the multilayer membrane i.e. stacking the three membranes into one layer, the cost of the multilayer of the membrane would become more expensive than that of using a single layer of membrane. Additionally, multilayer membrane resistance would become larger and reduce the permeation flux.



**Figure 1.** Mechanism of oil enlargement by permeating through the multilayer PTFE membranes [23].

Furthermore, in the reality, the membrane pore size is distributed but the previous researches did not highlight the influence of the pore size distribution as well as the membrane structure on the coalescence of the oil droplets when the commercial membranes were tested. Chiam et al. [24] have attempted to provide a framework for better understanding the effect of the cross-sectional pore size distribution of the membranes on the coalescence of the oil droplets by using the sponge-like structure of the polyvinylidene fluoride (PVDF) membranes. The tortuous structure of the membranes play significant role for coalescing the oil droplet.

The objective of this work is to examine the performance of asymmetric membranes in coalescing the oil droplets. The asymmetric membrane consists of two or more structural plane of non-identical morphologies with different pore sizes which can be fingerlike, sponge-like and macrovoids structures. The top layer of the membrane with smaller pore size is hypothesized to breakdown the oil droplets by deforming, squeezing and coalescing the oil droplets through the membrane pores, and growing at the bottom of the membrane surface which having larger pore sizes. The hypothetical mechanism is illustrated in Figure 2. Phase inversion method is used to fabricate the asymmetric membranes from PVDF and coagulated in various concentrations of ethanol solutions.



**Figure 2.** Hypothetical enlargement of oil droplets in the asymmetric structure of membrane.

## 2. Experimental methods

Polyvinylidene fluoride (PVDF, average MW  $5.3 \times 10^5$ ) in pellet form was purchased from Aldrich. N,N-dimethylacetamide (DMA), MERCK was employed as the polymer solvent. Lithium chloride (LiCl), Fluka was chosen as the additive in dope solutions. Ethanol (Sigma-Aldrich) was used as the non-solvent additive in the water coagulation bath. The crude oil used to simulate the feed solutions i.e. the Alkaline-Surfactant-Polymer (ASP) produced water was provided by the Sabah Oil and Gas Terminal (SOGT), PETRONAS.

The chemicals of the membranes consisted of PVDF, DMA and LiCl with the concentrations of 10, 88 and 2 wt.%, respectively. The appropriate amounts of the chemicals were mixed in a bottle; the bottle was capped and agitated at the temperature of  $50^\circ\text{C}$  for approximately 8 hours to obtain a homogeneous dope solution. The dope solution was stored in a cabinet for 3 – 4 days for air bubbles removal. The dope solution was transferred onto a clean glass plate, and immediately it was cast on the surface of the glass plate at the room temperature. A few with consistent cellophane tape layers was placed at the four sides of the glass plate in order to obtain the casted film thickness at about  $240 \mu\text{m}$ . The glass plate with the casted thin film was instantly soaked into the liquid coagulation baths. The liquid coagulation bath contained distilled water and ethanol. The concentrations of the ethanol used as the coagulants were 0, 10, 20 and 30 v/v %; thus the membranes were labelled correspondingly as PVDF0, PVDF10, PVDF20 and PVDF30. The nascent membranes were washed by using the distilled water. The membrane was air dried at approximately  $55^\circ\text{C}$  for about 2 – 3 hours. The SEM (Hitachi, S-3400 N) was used to observe the membrane morphologies. The sizes of 100 pores of one membrane sample were measured randomly at 10.0 kV of potential with magnification of 10 000x. The procedures used to conduct the coalescence experiment using the cross-flow membrane filtration were explained in our previous publication [25]. A constant flow rate of 1 L/min and the transmembrane pressure

varied at 0, 2 and 4 bars were tested. Each experiment was repeated at least two times in order to check the reproducibility of the results. The size distribution of the oil droplets in feed solution and permeates were analyzed by using a dynamic light scattering instrument (Malvern, Zetasizer Nano Series ZS), with the refractive index 1.59 and 1.330 for the material (oil) and water (diluted mineral water), respectively.

### 3. Results and discussion

#### 3.1. Effect of ethanol coagulant on the membrane morphology

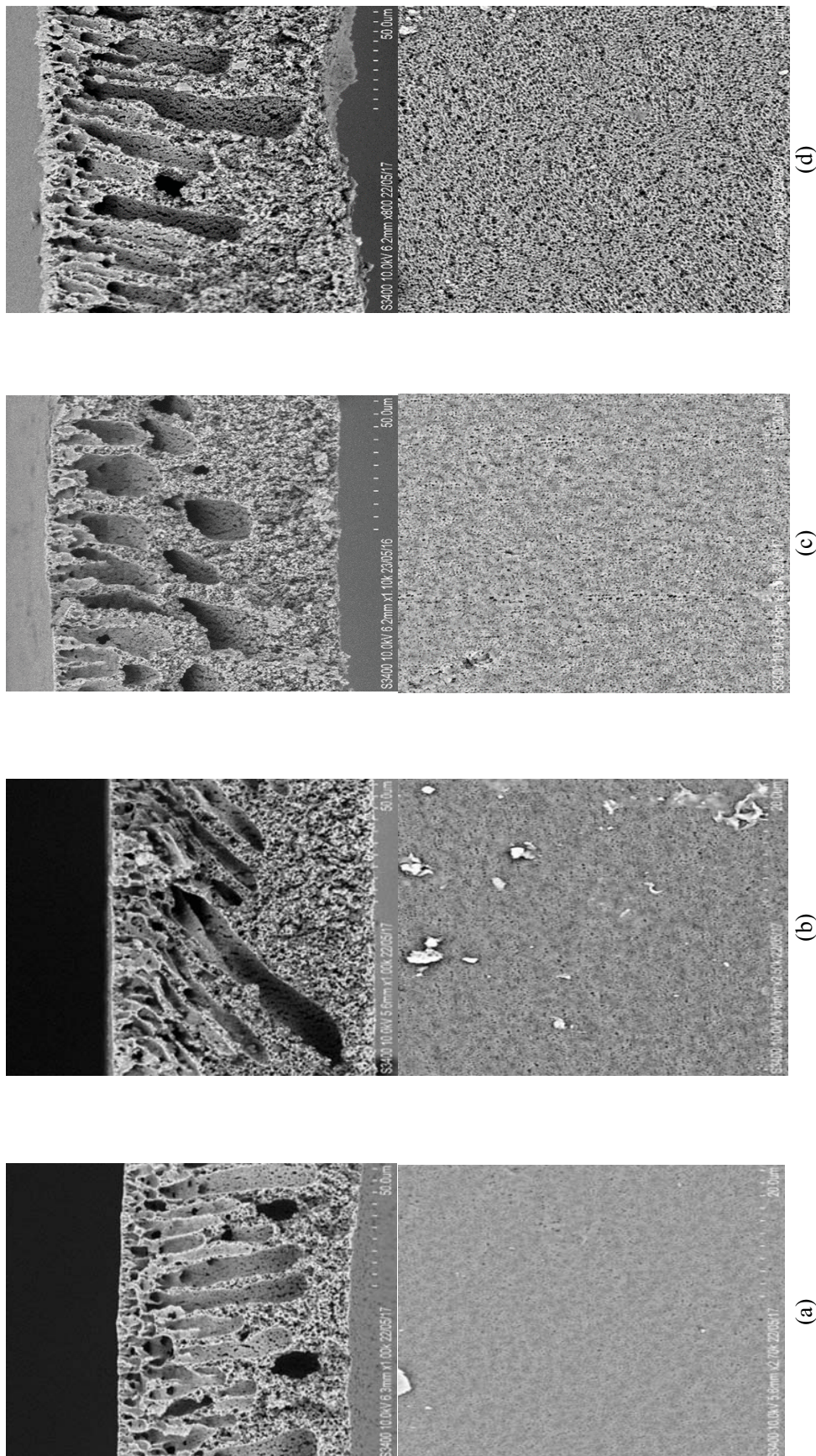
Coagulation rate during the phase inversion is significant to affect the membrane structure formation. The tendency of the membrane structure to change from a sponge-like structure to a fingerlike structure increases when the coagulation rate is faster [26-27]. Ethanol solutions were chosen as the coagulants to fabricate the PVDF membranes in this work. Figure 3 (a)–(d) correspondingly shows the micrographs of the cross-sections as well as the top surface of the PVDF membranes formed in the coagulation baths contained the ethanol with concentration varied from 0, 10, 20 and 30% (v/v). Figure 3 (a) shows the thin fingerlike structure formed in the PVDF0 membrane as the result of the interaction between the dope solution additive i.e LiCl and the distilled water is strong, which cause the fast diffusion of the LiCl into the water, and finally induced a rapid coagulation process. Figure 3 (b) shows the addition of ethanol in the coagulation bath has delayed the diffusion of LiCl into the coagulation bath, and hence reduced the coagulation rate. Few fingerlike structure diameters become larger in the PVDF10 membrane due to the slower coagulation. When the concentration of the ethanol was further increased in the coagulation bath, the thin fingerlike structure has almost disappeared while the size of the remaining pores is growing. Macrovoids were started to be formed near the top of the membrane surface and sponge-like structure is distinguishable near the bottom surface of the membrane in the PVDF20 and PVDF30 membranes, as shown in Figure 3 (c) and (d). The open pore structure became more visible on the membrane surface when the rate of coagulation reduced.

#### 3.2. Effect of membrane types

The diameters of the oil droplets in the feed solutions used in this work were ranging from 0.09 to 0.19  $\mu\text{m}$ . The mechanism of the oil droplet deformation and coalescence as hypothetically illustrated in Figure 1 is applicable when the pore size on the membrane surface (feed side) is smaller than the oil droplet size in the feed solution. In reality, the pore size is distributed on the membrane surface and the estimation of the number of pores that having smaller diameter than the oil droplets in feed solution is shown in Table 1. Although at least 50% of the pores of the membranes were larger than the diameters of the oil droplets in the feed solution, coalescence of the oil droplets did take place during the cross-flow membrane filtration process. The oil droplets might not be able to deform on the membrane surface when the membrane pore sizes were larger than the initial oil droplet sizes. The oil droplets were trapped into the larger open pore structure on the membrane surface and then deformed when flowed through the narrow tortuous paths. Similar findings have been reported in our previous study when the sponge-like structure PVDF membranes were tested [24].

**Table 1.** Number of membrane pores having diameter smaller than the oil droplets in the feed solutions.

Membrane	Number of Pores with diameter < 0.09 $\mu\text{m}$ (%)
PVDF0	47
PVDF10	26
PVDF20	19
PVDF30	0



**Figure 3.** SEM images of cross-section and membrane surface structures for (a) PVDF0, (b) PVDF10, (c) PVDF20 and (d) PVDF30.

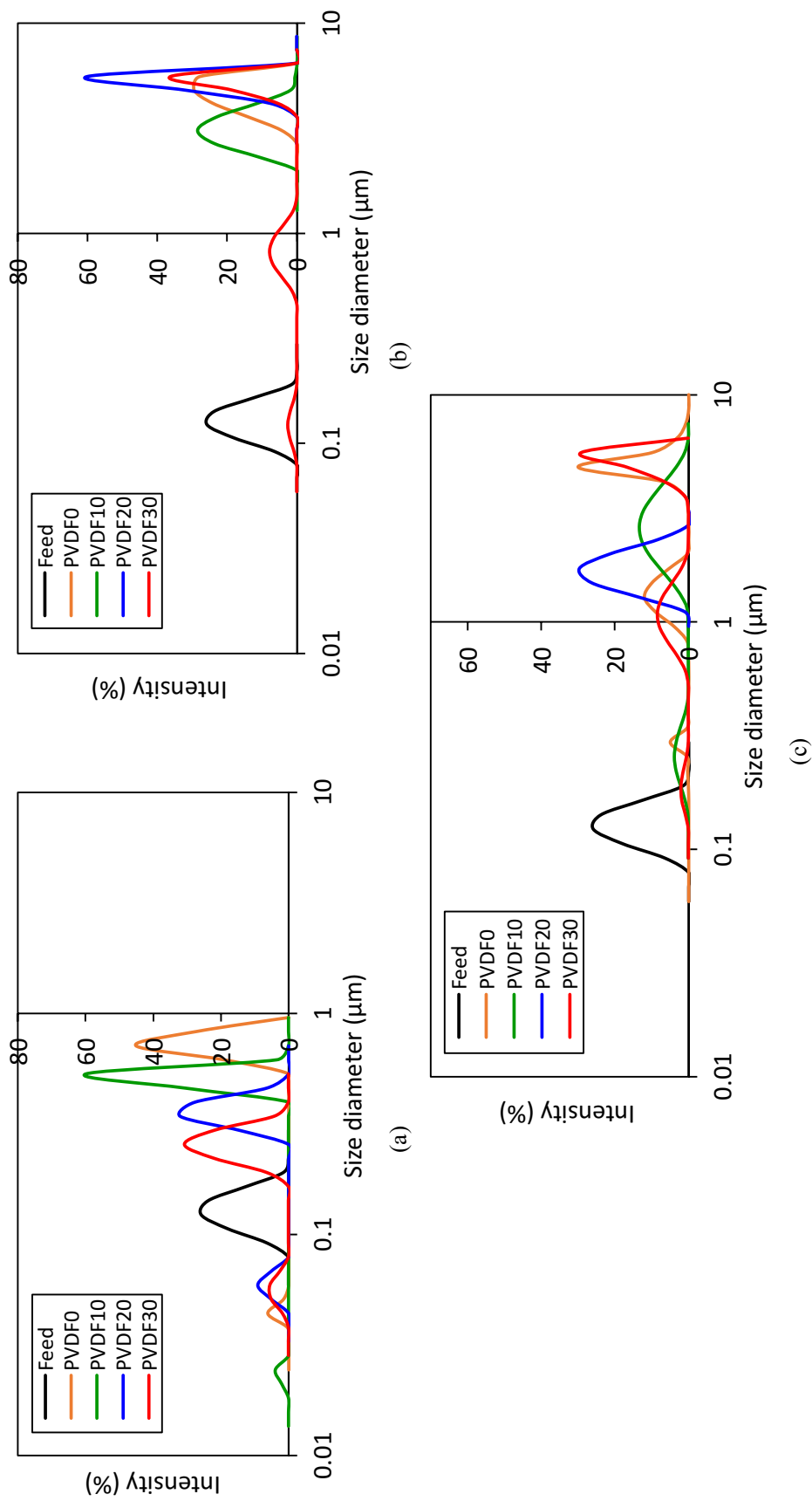
### 3.3. Effect of transmembrane pressures

The cross-flow membrane filtration process was used to test the fabricated asymmetric PVDF membranes for the coalescence of the crude oil droplets contained in the synthesized ASP produced water at different transmembrane pressures. For the first test, the produced water was pumped to the membrane permeation cell and the feed solution was circulated freely without pressurization; thus the transmembrane pressure was equal to zero. Figure 4 (a) shows the diameter distribution of the oil droplets in permeates for the transmembrane pressure is zero. As compared to the sizes of the oil droplets in the feed solution i.e. 0.09 – 0.19  $\mu\text{m}$ , the oil droplets at zero transmembrane pressure are slightly to coalesce to sizes of 0.2 – 1.0  $\mu\text{m}$  which comprise of 78 – 94% (by intensity) of the coalesced oil droplets in permeate. The permeations took place when the oil droplets wetted the membranes. The oil droplets were destabilised when the oil droplets travelled through the membrane pore structures and finally coalesced to each other to form larger droplets collected in the permeates. However, approximately 5 – 21% of the oil droplets in permeate having smaller diameters compared to the feed solution i.e. below 0.1  $\mu\text{m}$ ; it is deduced that some of the oil droplets in the rejection are broken down by the pumping effect.

When increased the transmembrane pressure to 2 bars, the diameters of the coalesced oil droplets in permeate are increased apparently, as shown in Figure 4 (b). At least 65% of the coalesced oil droplets in permeate having the diameters exceeding 1.0  $\mu\text{m}$ . The oil droplets with diameter below 0.1  $\mu\text{m}$  are almost disappeared. The pressurization is able to enhance the coalescence of the oil droplets. Similar result was found when the transmembrane pressure was further increased to 4 bars, as shown in Figure 4 (c). It is deduced that the surfactant films are sheared off from the oil droplets when forcing the oil droplets into the membrane pores, and hence to accelerate the membrane wetting and destabilisation of the oil droplets. Coalescence of the oil droplets occurs when they collide within the membrane pores. The coalesced oil droplets attach and grow at the larger pores on the bottom membrane surface. Nevertheless, it is noteworthy that when the transmembrane pressure was further increased to 4 bars, approximately 5% of the oil droplets having sizes ranged from 0.09 – 0.19  $\mu\text{m}$  as well as about 11 – 20% of the oil droplets having diameters between 0.2 and 1.0  $\mu\text{m}$ . This could be due to the acting force from the cross-flow stream swept the oil droplets away from the membrane surface before squeezing into the membrane pores. The oil droplets underwent breaking down by the pumping effect and coalesced to fairly large oil droplets during permeated through the pores.

## 4. Conclusions

This work examined the asymmetric PVDF membranes in coalescing the oil droplets from the simulated ASP produced water by using the cross-flow membrane filtration process. The initial diameter of the oil droplets in the simulated ASP water ranged from 0.09 to 0.19  $\mu\text{m}$ . Phase inversion technique was employed to prepare the asymmetric membranes by coagulating in the soaking baths containing different concentrations of ethanol i.e. 0 – 30 v/v %. Fingerlike structure was emerged when the coagulation bath consisted of the pure water. The diameter of the fingerlike structure increased when ethanol was added, and eventually macrovoids and sponge-like structures were visible when the concentration of the ethanol was further increased. The oil droplets deformed on the membrane surface when the membrane surface pores were smaller than the diameters of the oil droplets in the feed solutions. While for the membrane surface pores were larger than the diameters of the oil droplets, the oil droplets deformed when they were forced and flowed through the tortuous paths inside the membrane structure. The coalescence of the oil droplets took place remarkably when the filtration was pressurized, i.e. more than 65% of the coalesced oil droplets in permeate having the diameters exceeding 1.0  $\mu\text{m}$ .



**Figure 4.** The size diameter distribution of the oil droplets by intensity (%) in the permeates through the PVDF0, PVDF10, PVDF20 and PVDF30 membranes at transmembrane pressures (a) 0 bar, (b) 2 bars and (c) 4 bars.



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### 5. References

- [1] Olajire A A 2014 *Energy* **77** 963
- [2] Deng S, Bai R, Chen J P, Yu G, Jiang Z and Zhou F 2002 *Colloids Surf. A: Physicochem. Eng. Aspects*. **211** 275
- [3] Zhang R, Liang C, Wu D and Deng S 2006 *Colloids Surf. A: Physicochem. Eng. Aspects*. **290** 164
- [4] Guo J, Liu Q, Li M, Wu Z and Christy A A 2006 *Colloids Surf. A: Physicochem. Eng. Aspects*. **273** 213
- [5] Wang B, Wu T, Li Y, Sun D, Yang M, Gao Y and Li X 2011 *Colloids Surf. A: Physicochem. Eng. Aspects*. **379** 121
- [6] Deng S, Bai R, Chen J P, Jiang Z, Yu G, Zhou F and Chen Z 2002 *Sep. Purif. Technol.* **29** 207
- [7] Fakhru'l-Razi A, Alireza P, Luqman C A, Dayang R A B, Sayed S M and Zurina Z A, *J. Hazard. Mater.* **170** 530
- [8] Deng S, Yu G, Jiang Z, Zhang R and Ting Y P 2005 *Colloids Surf. A: Physicochem. Eng. Aspects*. **252** 113
- [9] Ge X, Yang J, Xu X and Gao J 2010 *Petrol. Sci. Technol.* **28** 1013
- [10] Alvarado V and Manrique E 2010 *Energies* **3** 1529
- [11] Cleveland C T 1999 *J. Am. Water Works Assoc.* **91** 10
- [12] Baker R W 2004 *Membrane Technology and Applications*. John Wiley & Sons Ltd.
- [13] Padaki M, Murali R S, Abdullah M S, Misdan N, Moslehyani A, Kassim M A, Hilal N and Ismail A F 2015 *Desalination* **357** 197
- [14] Chang I S, Chung C M and Han S H 2001 *Desalination* **133** 225
- [15] Abadi S R H, Sebzari M R, Hemati M, Rekabdar F and Mohammadi T 2011 *Desalination* **265** 222
- [16] Pagidi A, Saranya R, Arthanreeswaran G, Ismail A F and Matsuura T 2014 *Desalination* **344** 280
- [17] Hong A C, Fane A G and Burford R P 2002 *Desalination* **144** 185
- [18] Kiss Z L, Talpas L, Seres Z, Beszédes S, Hodúr C and László Z 2013 *Per. Pol. Chem. Eng.* **57** 21
- [19] Hong A, Fane A G and Burford R 2003 *J. Membr. Sci.* **222** 19
- [20] Hlavacek M 1995 *J. Membr. Sci.* **102** 1
- [21] Unno H, Saka H and Akehata T 1986 *J. Chem. Eng. Japan* **19** 281
- [22] Daiminger U, Nitsch W, Plucinski P and Hoffmann S 1995 *J. Membr. Sci.* **99** 197
- [23] Kawakatsu T, Boom R M, Nabetani H, Kikuchi Y and Nakajima M 1999 *AIChE J.* **45** 967
- [24] Chiam C K, Nurashiqin M, Zykamilia K, Ismail N M, Duduku K and Rosalam S 2019 *J. Appl. Membr. Sci. Technol.* **23** 25
- [25] Ramlee A, Chiam C K and Sarbatly R 2018 *AIP Conf. Proc.* **1958** 020004-1
- [26] Strathmann H and Kock K 1977 *Desalination* **21** 241
- [27] Jung J T, Kim J F, Wang H H, di Nicolo E, Drioli E and Lee Y M 2016 *J. Membr. Sci.* **514** 250