

Coalescence of Oil Droplets using Sponge-like Structure of Polyvinylidene Fluoride Membranes

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ABSTRACT

This work reports the effect of the membrane pore size distribution on the oil droplets size distribution in permeate using the polyvinylidene fluoride (PVDF) membranes. The sponge-like structures of the PVDF membranes were fabricated by phase inversion technique using 30% v/v ethanol aqueous solution as coagulation medium. Water and polyethylene glycol (PEG1000) were used as the pore forming additives in the dope solutions. Microfiltration was employed to coalesce the oil droplets at transmembrane pressure of 2.5 bar. Simulated alkaline surfactant polymer (ASP) produced water was tested as the feed solution. Results revealed that the PVDF membranes with sponge-like structure were formed. The additives in the dope solutions induced the membranes to become thicker due to more porous, spongy and resilient structure. The membrane pore sizes increased with the presence of the additives in the dope solutions especially when larger molecular weight of the additive i.e., PEG1000 was used. The mode of the oil droplets radius increased from 61.2 nm in the feed solution to 95.1, 356.2 and 1335 nm in the permeates by the corresponding membranes without additive, with water and PEG1000 as the additives. The membranes with larger pore sizes as well as more open structure were able to trap and coalesce more oil droplets which produced larger size of the oil droplets in the permeates.

Keywords ASP produced water, PVDF membranes, sponge-like structure, microfiltration; coalescence

1.0 INTRODUCTION

Alkaline-Surfactant-Polymer (ASP) is a promising tertiary method for Enhanced Oil Recovery (EOR) which has been proven with an excellent oil recovery up to 98% of the original oil in place (OOIP) in laboratory tests [1]. The ASP flooding technology in EOR applied in Daqing oil field, China is the largest at the present time [2] with more than 15 years ASP testing several pilots and different cases [3]. Other examples of the application of ASP EOR technology are Shengli and Karamay in China [4]; Taber South and Suffield in Canada; and West from Kiehl, Lawrence field Illinois and Cambridge Minnelusa in USA [5]. Nevertheless, the handling of the produced water from ASP process is challenging because the volume and the chemical residuals contained in the produced water are hardly separated. The surfactant helps to stabilize the oil droplets by reducing the oil-water interfacial tension and the zeta potential on the surfaces of the oil droplets. The skin layer surrounding the tiny droplets in the water emulsion prevents the oil droplets from uniting. Hence, the presence of the surfactant causes the produced water and ASP flooding becomes more

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complex and stable [9]. droplets without the surfactant films
 The management of the producedcollide together. The coalesced oil
 water becomes more challenging if droplets grow when they flow out from
 involves theoffshore ASP EOR the membrane pore on the downstream
 projects. Construction of the disposaside of the membrane.
 wells for the wastewater is unfavorableHydrophobic membranes such as
 as it is expensive. Overboard disposalpolytetrafluoroethylene (PTFE) with
 is commonly practiced especially forvarious pore sizes are normally tested
 the remote offshore locations.for destabilizing the oil droplets. Unno
 However, deoiling is a difficult work *et al* [11] reported that the oil
 because of the stringent regulatoryseparation rate increased with the
 standards for discharging producedmembrane pore size increased from 1
 water. For instance, the permitted oil to 10 m. Hlavacek [12] revealed that
 and grease limits for treated producedthe oil droplet size distribution in
 water discharge offshore in China,permeate showed the peak about 100
 Australia, US and North Atlantic m while the initial mean droplet size
 range between 10 and 50 mg/L [10],was 1.8m by using the polypropylene
 For the purpose of sustainability, reuse (PP) hollow fiber membrane with the
 of the produced water rejection pore size of 0.2m. However,
 is an attractive option for offshore ASPEnlargement on the oil droplets was not
 EOR as this can reduce the significant when PP with effective pore
 environmental issue and lower the costsize 0.05m was used for initial oil
 of chemicals. The crude oil that droplet size distribution from
 emulsified in the produced water isapproximately 5 to 10m [13], while
 valuable and worth to be recovered. the larger pore size of the PTFE
 Microfiltration by using membrane, i.e., 5m was able to
 hydrophobic membranes have beenenlarge the oil droplet sizes from the
 successfully tested for destabilizing theinitial droplet sizes less thanm2
 oil-water emulsion [14]. The [15]. From the findings in the
 hypothetical mechanism of the oil literature, the effect of membrane pore
 droplet coalescence [12] is illustrated size on the oil droplet coalescence
 in Figure 1. The surfactant films becomes significant if the membrane
 covered the oil droplets prevent the pore size exceeds 0.2m while smaller
 droplets from uniting in the feed. The pore size, e.g., 0.05m has no
 feed contains the oil droplets isessential effect on the coalescence.
 brought into a direct contact with theHowever, the effect of the membrane
 membrane surface. The oil droplets pore size on the oil droplets
 tend to attach the membrane surface coalescence is not clear as
 when the membrane surface isfact, the membrane pore size may
 hydrophobic. The oil droplet deformed distribute from 0.05 to 10
 and squeezed into the membrane poreFurthermore, the structures of the
 when the feed is pressurized. Thecommercial membranes tested in the
 surfactant film is stripped off and literature are not consistent. For
 collapsed when the oil droplet is forcedinstance, in reality, the membrane
 to flow into the narrow pore. Thus, the structure is tortuous instead of a
 oil droplet is destabilized and straight cylindrical shape as shown in
 coalescence happening when twoFigure 1 [14].

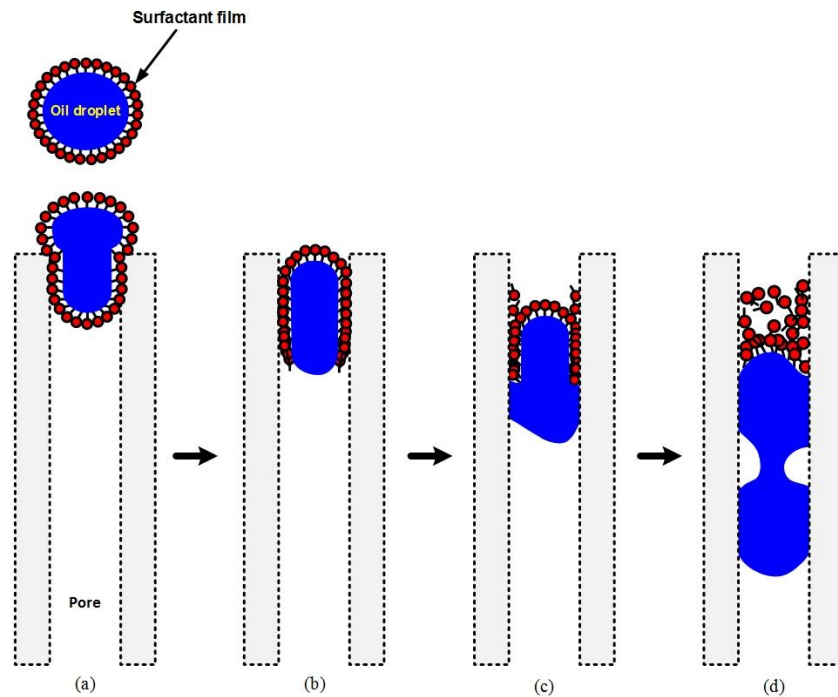


Figure 1 Hypothetical oil droplet coalescence through membrane pore deformation (b) squeezing (c) surfactant film collapsing (d) coalescence and c

This work aims to gain a better understanding for the effect of additives. The compositions of the dope solution formulation were shown in Table 1. The appropriate amounts of chemicals were mixed in a closed bottle and stirred continuously on a hot plate at 50°C for 6 hours for producing a homogeneous solution. The dope solution was remained in a calorimeter three days for bubbles removal. The dope solution was poured carefully onto a clean and smooth glass plate; and immediately the solution was cast by using a knife at room temperature. Adhesive tape with thickness about 0.5 mm was used to control the thickness of casting. The glass plate with the casted film was promptly immersed into a 30% v/v ethanol solution coagulation bath for 5 s and next into a water bath for 4 hours. The membranes were washed thoroughly with distilled water and then dried overnight at 23°C.

2.0 METHODS

2.1 Membrane Fabrication

Polyvinylidene fluoride supplied by Sigma-Aldrich in pellet form, was used to fabricate the membranes. dimethylacetamide (DMA) supplied by Acros Organics, was used the polymer solvent. Polyethylene glycol with molecular weight 1000 purchased from Fluka, and distilled

water were used as the dope solution. The compositions of the dope solution formulation were shown in Table 1. The appropriate amounts of chemicals were mixed in a closed bottle and stirred continuously on a hot plate at 50°C for 6 hours for producing a homogeneous solution. The dope solution was remained in a calorimeter three days for bubbles removal. The dope solution was poured carefully onto a clean and smooth glass plate; and immediately the solution was cast by using a knife at room temperature. Adhesive tape with thickness about 0.5 mm was used to control the thickness of casting. The glass plate with the casted film was promptly immersed into a 30% v/v ethanol solution coagulation bath for 5 s and next into a water bath for 4 hours. The membranes were washed thoroughly with distilled water and then dried overnight at 23°C.

Table 1 Dope formulation for membranes

Membrane	Formulation (wt.%)	
PVDF1	PVDF/DMA	: 10/90
PVDF2	PVDF/DMA/water	: 10/88/2
PVDF3	PVDF/DMA/PEG solution*	: 10/88/2

* The PEG solution consists of 16.5 wt.% PEG and 83.5 wt.% distilled water.

2.1 Membrane Characterization

2.2.1 Membrane Structural Morphology

The structural morphology of the membranes was observed by using a scanning electron microscopy (SEM, Hitachi, S3400N) after the membrane samples were fractured in the liquid nitrogen and sputtered with a thin gold film.

pores and dissolved in the water. The water replace the isopropyl alcohol inside the membrane pores. After 30 minutes, the membrane was immersed in a new water bath and rinsed. The

excess water droplets on membrane surfaces were removed by using a paper tissue. The membrane weighted. The porosity of the membrane was determined as follows:

$$\text{Porosity} = \frac{W_w - W_d}{\rho_w} \quad (1)$$

2.2.2 Thickness Measurement

The membrane thickness was measured by using a digital micrometer (RS 70529, China), with precision ± 0.001 mm, at 30 locations of the membrane and its average value and the standard deviation were calculated.

where W_w is the wet membrane weight, W_d is the dry membrane weight, ρ_w is the water density (0.9973 g/cm^3 at 25°C) and ρ_p is the PVDF density (1.78 g/cm^3).

2.2.4 Pore Size Measurement

The membrane pore sizes were measured directly by using the SEM (Hitachi, S3400N). The cross section images of the membranes were observed at 10.0 kV of potential with magnifications of 6500x. The sizes of 100 membrane pores were randomly selected and measured for each membrane formulation.

2.2.3 Porosity Measurement

The membrane porosity is defined as the volume of the pores divided by the total volume of the membrane. Gravimetric method was used to determine the porosity of membranes. Isopropyl alcohol (IPA) was employed to wet the membrane pores. First, the dried membrane was immersed in the isopropyl alcohol for 30 minutes. The isopropyl alcohol entered the filled all the membrane pores. Next, the wetted membrane was immediately transferred into a distilled water bath and the membrane was immersed for another 30 minutes. The isopropyl alcohol diffused out from the

2.3 Microfiltration Experiments

2.3.1 ASP Solution Preparation

A volume of 1 L of mineral water was prepared by using distilled water with the addition of 1600 mg/L NaCl; 2600 mg/L NaHCO_3 ; 300 mg/L Na_2CO_3 ; 40 mg/L Na_2SO_4 ; 40 mg/L CaCl_2 and 40

mg/L MgCl₂ To synthesize the oily wastewater produced from alkaline surfactant polymer (ASP) flooding, 1500 mg/L crude oil, 350 mg/L sodium dodecylbenzene sulphonate, 800 mg/L sodium hydroxide and 400 mg/L polyacrylamide were added into 996.95 g of the mineral water. The mixture in a bottle was placed in a shaker with water bath temperature 45°C and mixing rate at 120 rpm for 24 h.

2.3.2 Filtration Setup

A microfiltration as shown in Figure 2 purchased from Advanced Membrane Technology Research Center, Universiti Teknologi Malaysia, was employed to examine the coalescence of oil droplets. The membrane with an effective area of 17.35 cm² was placed into the permeation cell. The synthesized ASP produced water was placed in the feed tank. The feed was pumped into the permeation cell. The experiments were conducted at a constant feed flow rate of 1 L/min and transmembrane pressure of 2.5 bar. The permeate was collected into a beaker. The flux (was calculated as follows:

$$J = \frac{m}{A \cdot t} \quad (2)$$

where m is the mass of permeate, A is the effective membrane area and t is the time of collecting the permeate.

2.3.3 Oil Droplet Size Analysis

A Malvern Zetasizer Nano ZS DLS Nano Zen 3600 which was a dynamic light scattering instrument was used to determine the sizes of the oil droplets in the feed water and permeate. The refractive index was 1.59 for the oil and 1.330 for the water.

3.0 RESULTS AND DISCUSSION

3.1 Membrane Properties

3.1.1 Morphology Study

SEM micrographs of the PVDF membranes coagulated in 30% v/v ethanol were shown in Figure 3. The PVDF membranes with spongy structure have been successfully produced by using the ethanol coagulation bath. Coagulation medium essentially influences the membrane formation during phase inversion process. The cross section of the membrane morphology tends to become spongy structure when the coagulation rate is slower. In this case, the presence of ethanol in the coagulation bath has reduced the water activity in the coagulation bath; thus, the diffusion of the DMAC into the coagulation bath is delayed and eventually spongy structure is formed. Similar observations have been found in the literature when ethanol is added in the coagulation baths [16, 18].

3.1.2 Porosity

Table 2 presents the porosity of the PVDF membranes measured by using the Equation (1). Compared to the PVDF1 membranes, the additives in the dope solutions have increased the porosities in the PVDF2 and PVDF3 membranes. The membranes having the highest porosity when using PEG1000 as the additive. The family of PEGs has been known as the pore forming agents in membranes [19, 20].

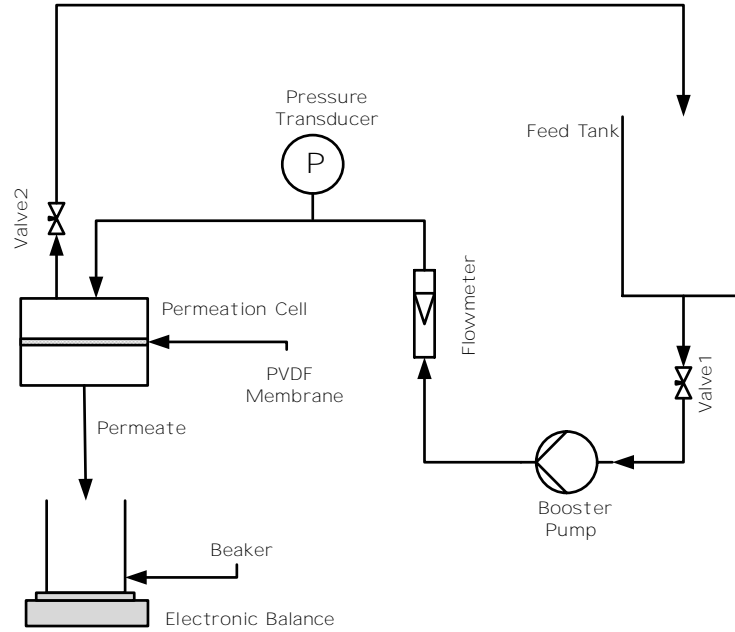


Figure 2 Microfiltration Setup

3.1.3 Thickness

The thickness of the membranes were measured by using the digital micrometre. The average thickness of the membranes is shown in the Table 2. Compared to the PVDF1 membranes, the thicknesses of PVDF2 and PVDF3 membranes are increased approximately 10 and 28% respectively. It is deduced that the thickness increase simultaneously as shown in Table 2.

3.1.4 Pore Size Distribution

The membrane pore sizes were measured directly by using SEM. Figure 4 illustrates the pore size distribution of the PVDF membranes. The highest

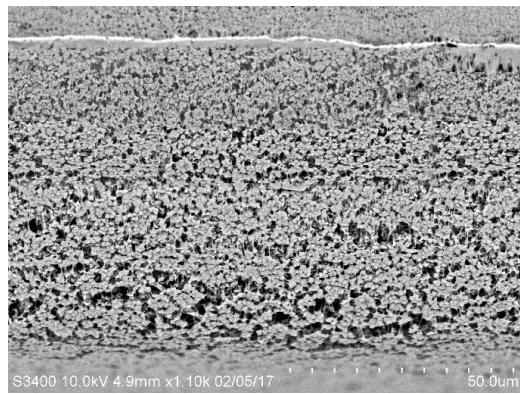
number of pores in PVDF1 membrane having the pore sizes about 40% of pores; in PVDF2 is between 0.90 and 1.5 micrometre occupied by about 33%; while 28% of pores in PVDF3 having sizes of between 0.90 and 1.5 micrometre are within 1.5 micrometre. The pores are formed when the additives diffused out from the thin film (dope solution) and mix into the coagulation bath. The distribution of the pore sizes in the PVDF3 is larger than that in the PVDF2; because the molecular weight of the additive used in the PVDF3 i.e. PEG1000 is larger than that of the additive used in the PVDF2 which is the water.

3.2 Coalescence of Oil Droplets

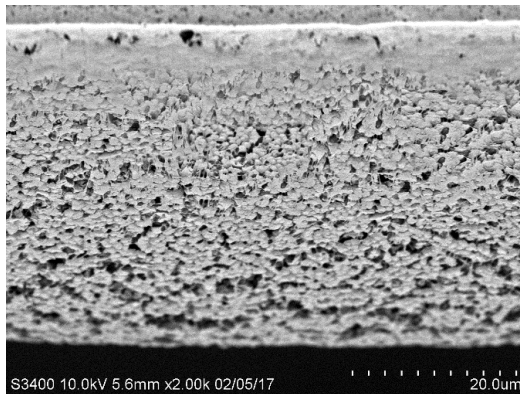
The permeation flux for each

Table 2 Membrane Properties

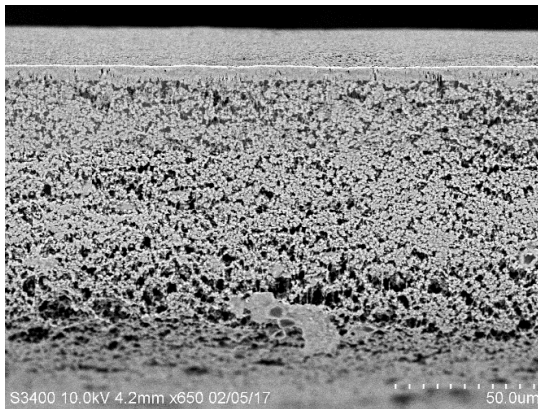
Membrane	Porosity (%)	V j k e m p g u	Morphology
PVDF1	48.2	98 ± 6.6	Sponge-like
PVDF2	58.1	108 ± 8.5	Sponge-like
PVDF3	63.6	126 ± 4.8	Sponge-like



(a)



(b)



(c)

Figure 3 SEM images of the cross-section structures of the membranes, (a) PVD PVDF2 and (c) PVDF3

membrane formulation is determined by pressurizing the feed solution at 2.5 bar. Figure 5 shows the permeation fluxes for the membranes over time. By adding the additives in the membrane formulation solutions, the

fluxes increase in the order PVDF3 > PVDF2 > PVDF1 membranes. This indicates that the open pore structures on the membrane surface are more when adding water and PEG into the membrane dope solutions. The permeation fluxes values are in agreement with the data reported in Table 2 and Figure 4; that is, the membranes formulated from additives are spongier with larger porosity and more open structure as well as thickness increases. It is noteworthy that the effect of membrane thickness on the flux is lesser as compared to the effect of open pore structure.

The oil droplet sizes in the permeate were measured by using the dynamic light scattering instrument. Figure 6 exhibits the oil droplet size distribution in the permeate from the microfiltration through PVDF1, PVDF2 and PVDF3 membranes. Based on the statistical analysis, the mode of radius oil droplets in the feed ASP solution is 61.2 nm with intensity 25.8%. The mode of the radius of oil droplets in permeates increased to 95.1 nm by PVDF1, 356.2 nm by PVDF2 and 1335 nm by PVDF3 with the corresponding intensities 30.8, 22.1 and 28%. Compared to the oil droplets size distribution in the feed ASP produced water, the oil droplet sizes distribution are obviously shifted to the right of the graphs which indicated that the coalescence of the oil droplets occurred during the microfiltration process.

The oil droplet enlargement by the membranes is following the order PVDF3 > PVDF2 > PVDF1. A model of the oil droplet coalescence is thus developed as illustrated in Figure 7. The open pore structure increases in PVDF2 and PVDF3 membranes which may lead to the pore sizes exceeding the diameters of the oil droplets.

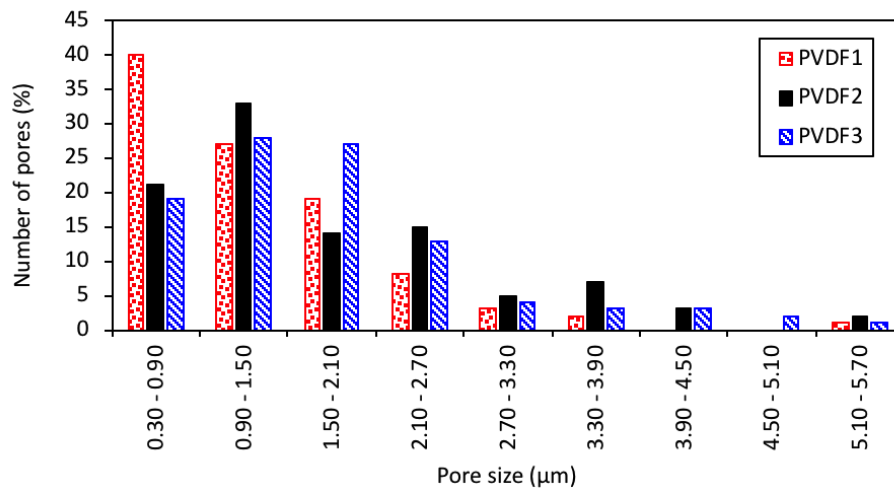


Figure 4 Pore size distribution of the membranes

Hence, the oil droplets will be trapped easier to be escaped from the trapping into the open pore structure at the membrane surface without from the cross flow operation when the deformation. Unlike the membrane with smaller open pore structure shown in Figure 1 which is used (Figure 7 (a)). Figure 7 (b) shows the larger open pore structure, in reality, the pores are tortuous in the sponge-like structure membranes. The resulting in the larger coalesced oil droplets are trapped in the pore structure. Due to the coalescence of the more oil droplets occurred within the membrane tortuous paths by the applied pressure, the permeation fluxes for the PVDF2 and PVDF3 are visibly collapsed and the droplets combined to become a larger droplets. The oil droplets in the feed channel are

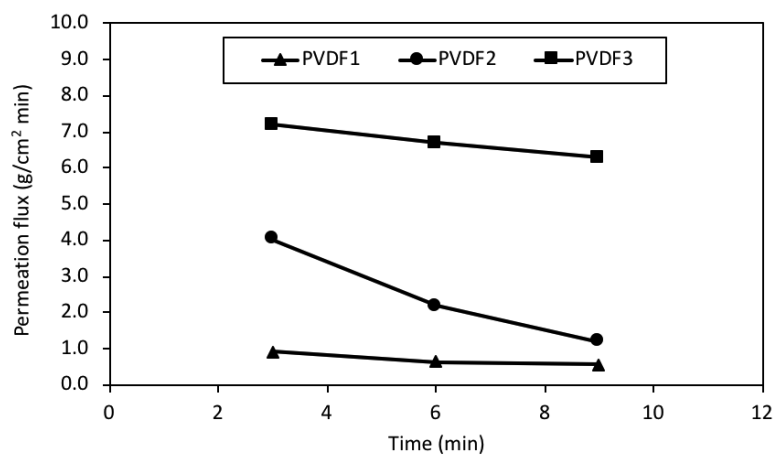


Figure 5 Microfiltration permeation fluxes as function of time at transmembrane 2.5 bar

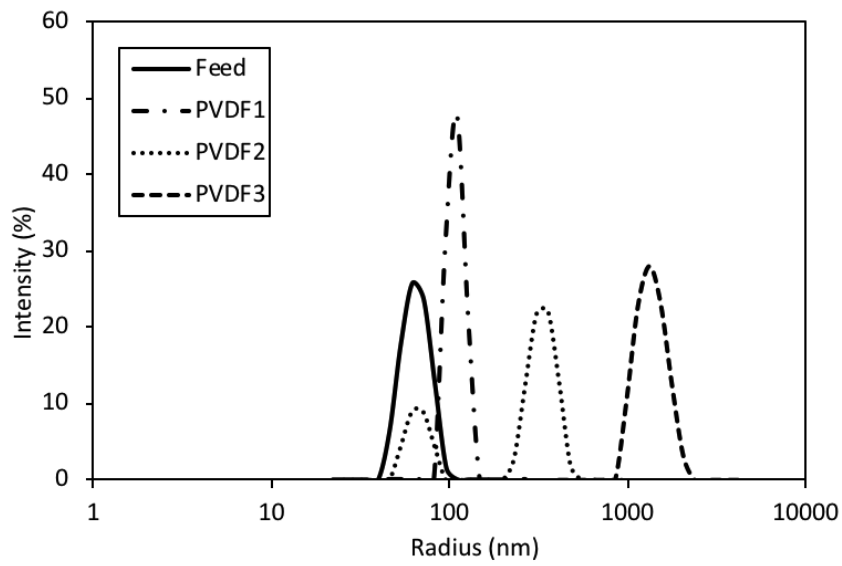


Figure 6 The distribution of the oil droplet size (radius) by intensity (%) in the solution and permeates through the membranes

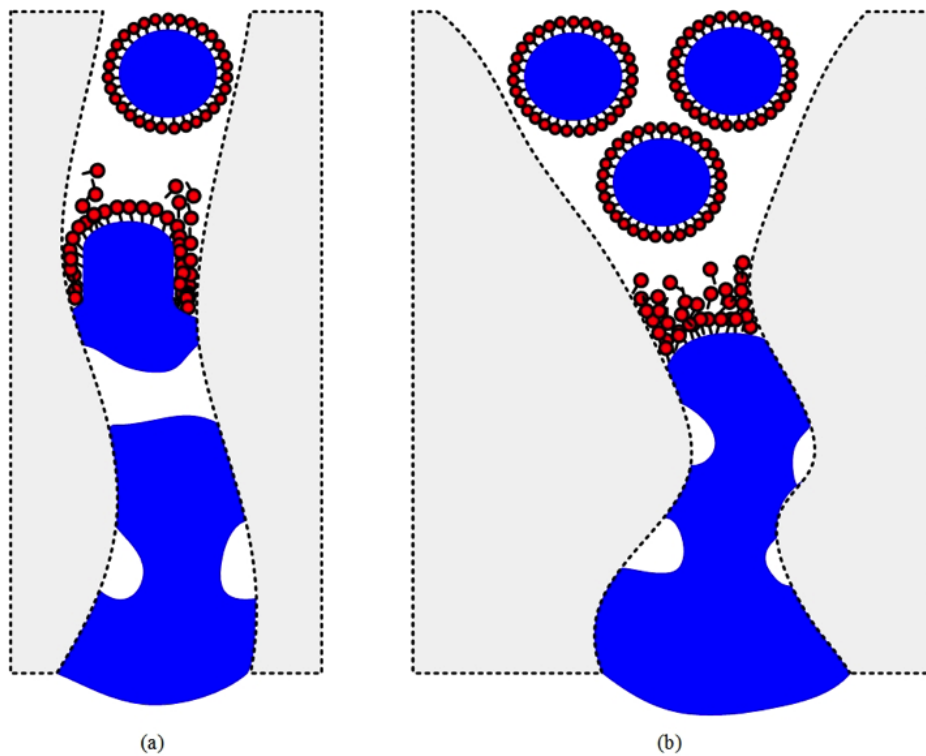


Figure 7 The coalescence of the oil droplets in the tortuous paths of membranes for the initial size of oil droplets smaller than the membrane surface (a) membrane surface with smaller pore size (b) membrane surface with large pore size

4.0 CONCLUSIONS

PVDF membranes with sponge structure have been successfully fabricated by using phase inversion [3] technique and coagulating in the water bath containing 30% v/v ethanol solution. Three types of membranes were formulated i.e. without additive [4] (PVDF1), with water (PVDF2) and PEG1000 (PVDF3) as the additives in the dope solutions. The membrane thickness, porosity and pore size increased in the order of the membranes PVDF3>PVDF2>PVDF1. The additives in the dope solutions caused the membrane structures [5] become more porous, spongy and resilient. The PVDF3 membrane having the larger pore size range than the PVDF2 because the molecular weight of the PEG was larger than that of the water. With the larger pore size [6] range and more open pore structure in the PVDF3 membrane, more oil droplets were trapped and forced to form larger oil droplets in the permeate.

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REFERENCES

- [1] R. Fortenberry. 2013. Experimental demonstration and improvement of chemical EOR techniques in heavy oils. M.S Thesis, University of Texas at Austin.
- [2] G. Shutang, L. Huabin, Y. Zhenyu, M.J. Pitts, H. Surkalo, K. Wyatt. 1996. Alkaline/surfactant/polymer pilot performance of the West Central Saertu, Daqing oilfield. *SPE Reserv. Eng.* 11: 181-188.
- [3] V. Alvarado, E. Manrique. 2010. Enhanced oil recovery: An update review. *Energies* 3: 1529-1575.
- [4] Q. Qi, H. Gu, D. Li, L. Dong. 2000. The pilot test of ASP combination flooding in Karamay oil field. In: Paper SPE 64726 presented at the 2000 SPE International Oil and Gas Conference and Exhibition in China, 7-10 November, Beijing, China.
- [5] T. Chen, G. Zhang, J. Ge, H. Yang. 2013. The research on weak alkali ASP compound flooding system for Shengli heavy oil. *Adv. Petrol. Explor. Dev.* 5: 106-111.
- [6] S.R. Clark, M.J. Pitts, S.M. Smith. 1993. Design and application of an alkaline surfactant/polymer recovery system to the west Kiehl field. *SPE Adv. Technol. Series*: 172-179.
- [7] B. Seyler, J. Grube, B. Huff, N. Webb, J. Damico, C. Blakley. 2012. Reservoir characterization of Bridgeport and Cypress sandstones in Lawrence field Illinois to improve petroleum recovery by alkaline-surfactant polymer flood. *Ener. Technol. Data Exchange* 2012: 12-21.
- [8] C.S. Gregersen, M. Kazempour, V. Alvarado. 2013. ASP design for the Minnelusa formation under low salinity conditions: Impacts of anhydrite on ASP performance. *Fuel* 105: 364-382.
- [9] O.O. Foyeke, J.B. Diane. 1998. Influence of interfacial properties of lipophilic surfactants on water-in-oil emulsion stability. *Colloid Interf. Sci.* 197: 142-150.

- [10] Rafiq, P.D Alireza, C.A. Luqman, R.A.B. Dayang, S.M. Sayed, Z.A. Zurina. 2009. Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* 170: 530-551.
- [11] H. Unno, H. Saka, T. Akehata. 1986. Oil separation from oil water mixture by a porous poly(tetrafluoroethylene) (PTFE) membrane. *J. Chem. Eng. Japan* 19: 281-286.
- [12] M. Hlavacek. 1995. Break of oil-in-water emulsions induced by permeation through a microfiltration membrane. *Membr. Sci.* 102: 1-7.
- [13] U. Daiminger, W. Nitsch, P. Plucinski, S. Hoffmann. 1995. Novel techniques for oil/water separation. *J. Membr. Sci.* 99: 197-203.
- [14] T. Kawakatsu, R.M. Boom, H. Nabetani, Y. Kikuchi, M. Nakajima. 1999. Emulsion breakdown: Mechanisms and development of multilayer membrane. *AIChE J.* 45: 967-975.
- [15] A. Hong, A.G. Fane, R. Burford. 2003. Factors affecting membrane coalescence of stable oil-in-water emulsions. *J. Membr. Sci.* 222: 103-9.
- [16] P. Sukitpaneemit, T.S. Chung. 2009. Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology. *J. Membr. Sci.* 340: 192-205.
- [17] D. Wang, K. Li, W.K. Teo. 1999. Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes. *J. Membr. Sci.* 163: 211-220.
- [18] S.P. Deshmukh, K. Li. 1998. Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fiber membranes. *J. Membr. Sci.* 150: 75-85.
- [19] D. Hou, H. Fan, Q. Jiang, J. Wang, X. Zhang. 2014. Preparation and characterization of PVDF flat sheet membranes for direct contact membrane distillation. *Sep. Purif. Technol.* 135: 211-222.
- [20] E. Saljoughi, M. Amirilargani, T. Mohammadi. 2010. Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes. *Desalination* 262: 72-78.