Advanced Aeration Using Finned Panel Spacer For Fouling Control In Produced Water Membrane Filtration

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Abstract. Treatment of produced water (PW) is a challenge largely due to its form as stable oil/water emulsion. Membrane technology has shown promise in treating PW by efficiency removing micron-size oil droplets, but still suffers from major obstacle of membrane fouling. Many approaches have been introduced to mitigate membrane fouling including employing air bubbles (aeration) which improve hydrodynamics for scouring off the foulants. Despite offering some advantages, it still constrained by poor contact and distribution toward membrane surface. Thus, those limitations became highly concerned, and will be handled in this study by applying new finned spacer. The spacer encourages air bubbles flow path homogenously covering whole membrane surface. The filtration tests were performed using lab-made Polysulfone (Psf) flat-sheet membrane assembled into a flat-sheet panel. The results show excellent effect of aeration using finned panel spacer by performing higher flux and rejection. The bubbles are well distributed and homogeneously projected on the membrane surface by the finned spacer. Thus, the objective to mitigate fouling can be obviously achieved.

1. Introduction

Oil and gas industries are paramount significance in modern civilization. During extraction and processing, they generate large volume of oily waste water which contains various organics and inorganics [1]. Produced water (PW) is defined as water extracted from subsurface containing oil and gas. In old wells, its volume can reach of about 10 times of the produced oil [2] and its fraction is larger as the aging of the wells. It has different characteristics by well to well [3]. It consists of around 70% of total waste water during oil production [3]. In PW, oil is dispersed in water, stabilized by surfactant [4], which makes its treatment challenging. PW also contains suspended solids and dissolved organics [4].

Various methods have been used to treat PW, including both of conventional and advanced methods. One of the advanced methods is membrane technology that has long been implemented for treatment of PW [5,6]. Although it brings promises, it still suffers from membrane fouling [7]. Currently, all membrane based process require rigorous pre-treatment before used as polishing step in PW treatment [5]. Polymer material that commonly used to prepare MF/UF are polysulfone (Psf), polyethersulfone (PES), PVDF, PAN and cellulose acetate (CA) [8]. Among them, Psf has high mechanical stability over wide range of temperatures from -100 °C to160 °C. It has excellent chemical and physical properties e.g thermal and chemical stability, mechanical strength and oxidative resistance. Thus, Psf becomes preferred membrane material especially for water treatment in ultrafiltration system [9]. Moreover, Psf also offers many advantages: (i) highly resistant to mineral acids, alkali and electrolytes in pH ranging
2 to 13, (ii) resistant to oxidizing agent, so they can be cleaned by bleaches (iii) resistant to surfactants and hydrocarbon oil (iv) soluble in solvent (DMAc and NMP), make it applicable for conventional phase inversion method (v) good mechanical strength and permeability (vi) easily to modify properties through polymer blending.

Air bubbling has become a standard method for pressure driven membrane fouling control [10–12]. The air bubbles help to restrict foulant deposition and suppress cake layer build-up to maintain permeability [11,13]. Despite many advantages, air bubbles scouring still has few limitations: producing weak shear rates and the impact reaches plateau over at certain air supply rate [11,14]. This work focuses on maximizing the impact of air bubble for membrane cleaning, preferably under moderate velocity [15]. Bubble size and its number/amount must be optimized to give desirable hydrodynamic conditions and at the same time to minimize energy consumption [16]. Another factor considered is the effect of turbulences in membrane process. Turbulence flow regime can suppress concentration polarization. It can be built up by employing two-phase flow involving air bubbles [16]. Thus, it needs to be evaluated and optimized thoroughly.

Recently, an attempt has been proposed via introduction of spacer in the module assembly to enhance the effect of air bubbles for membrane fouling control. The spacer promotes bubble oscillation and random movement which effectively decline membrane fouling by improving turbulences, diminishing concentration polarization and increase mass-transfer rate [17]. Such system was found effective, especially when coupled with elevated liquid cross flow velocity. The bubble flow paths also highly depend on cross flow of the feed liquid [17]. This method is quite practical but exhibits higher energy compared to the standard aerated panel (without spacer), because the need of high liquid cross-flow velocity to encourage air bubble distribution. An attempt to maximize contact of air bubbles and membrane has also been introduced via a tilted panel [10]. The system is found to be effective for one sided membrane, low in footprint but requiring an impractical switching mode to enable intermittent aeration to both sides of panel. The most preferred is indeed to use a conventional of vertical panel membrane due to its easy handling and small footprint.

Introducing of spacer in membrane module assembly is found effective to distribute air bubble but still highly depends on feed cross-flow velocity that can inflate energy consumption. In this study, a new system is proposed to maximize the role of air bubble (aeration) in membrane fouling control by employing a novel finned spacer. The fins are placed in between two adjacent vertical panels that help to encourage air bubble flow path in order to get excellent bubble flow trajectory distribution on the membrane surface and better bubble-surface contacts. This project proposes to optimize the role of air bubbling for membrane fouling control on vertical membrane panel via introduction of finned spacer.

2. Material and method

Membrane preparation, characterization and module assembly

Polysulfone (Psf) (BASF, Mn 22,000) polymer membrane, was prepared via wet phase inversion method. Polyethylene glycol (PEG) (Sigma-Aldrich Mw 1,0000) as additive, DMAc (Sigma-Aldrich) as solvent and Deionized water as non-solvent. The dope solution composition was 15%, 1% and 84% respective to Psf, PEG and DMAc. The mixture was mixed up by magnetic stirrer at 60 °C for 36 hours to obtain homogeneous solution. The homogenous solution then was degassed for 24 hours to release entrapped air bubbles. The solution was casted with casting knife at 0.22 mm wet-thickness followed by directly soaked in non-solvent. The produced Psf membrane was kept in wet until assembled into a filtration panel. The prepared membrane will be characterized by contact angle to measure its hydrophilicity.

Membrane porosity (\(\delta\)) was measured using gravimetric method and the value was estimated using (Eqs 1&2).

\[
\delta = \frac{V_{pore}}{V_{membrane}} \times 100 \quad (1)
\]

\[
V_{pore} = \frac{M_{wet} - M_{dry}}{\rho_{wetting \text{ agent}}} \quad (2)
\]
Where, $V_{pore}$ is volume of membrane pores, $M_{wet}$ and $M_{dry}$ indicate wet membrane weight and dry membrane weight, the applied wetting liquid was n-butanol with $\rho = 0.92 \text{ g/cm}^3$.

To be practically functional, membrane was assembled into a membrane filtration panel with effective area 10 cm x 14 cm (140 cm$^2$) (Figure 1). Two panels were required to build up one module system. One membrane sheet was glued on frame using oil-resistant glue to prevent any leaking due to the use of PW as feed liquid. After passing leaking test, two panels were arranged in parallel, sandwiching tightly a finned spacer between them. The packing was set tight to prevent air bubble lost from the module system. Thus, from that arrangement air bubbles will totally distribute inside the module.

Produced water

PW sample was collected from one of oil production unit in Malaysia. Since the properties characteristic of PW changes over time and to preserve the emulsion, PW sample was collected at once and was kept at around 4°C in dark room. PW characteristic is provided in Table 1.

Finned spacer

Finned spacer was made using PMMA/acrylic having 73° contact angle which means having hydrophilic properties. Fins were arranged horizontally on spacer stand. Finned spacer was placed in between two adjacent membrane panel.

**Table 1. PW characteristic**

| Items                       | Amount         |
|-----------------------------|----------------|
| Conductivity                | 2000 µs cm$^{-1}$ |
| pH                          | 6              |
| Turbidity                   | 79.4 NTU       |
| COD                         | 2060 mg L$^{-1}$ |
| Total oil and grease (TOG)  | 11.27 mg L$^{-1}$ |
| Total nitrogen (TN)         | 36 mg L$^{-1}$  |
| Total phosphor (TP)         | 12.8 mg L$^{-1}$ |

![Image of membrane module](image)

**Figure 1.** Membrane module

Experimental set-up

The membrane filtrations were run in submerged and constant-pressure system (Figure 2). A vacuum pressure pump also be used to exert vacuum condition and drive the membrane filtration. The $\Delta P$ was kept constant at -0.1 bar by adjusting control valve. The permeate has been collected semi-batch wise for every operation cycle (9.5 min filtration and 0.5 min relaxation). After permeate volume was measured, the permeate was returned back into the tank to maintain feed liquid level.

The permeance flux ($J$) was calculated from permeate flow rate measured every 10 min for 12 cycles. Permeability ($L$) can be attained from flux (Eqs 3&4). The permeability profile indicates the effectivity of membrane operation and detects fouling occurrence.

$$J = \frac{V}{A \cdot t} \quad (\text{L/m}^2\text{h}) \quad (3)$$

$$L = \frac{J}{\Delta P} \quad (\text{L/m}^2\text{bar}) \quad (4)$$

Where, V is permeate volume (l), A effective membrane area (m$^2$), t filtration time (h), and $\Delta P$ trans-membrane pressure (bar).
Figure 2. Experimental Set-up

Rejection was calculated using Eqs 5:

\[ R(\%) = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \] (5)

Where, \( C_p \) and \( C_f \) is permeate and feed parameters.

3. Result and discussion

Membrane characteristics

Membrane characteristics in Table 2 indicate that it is suitable for PW treatment. Contact angle test employs water drops on membrane surface then at certain magnification it will get the degree of water drop toward membrane surface. Angles of less than 90° means hydrophilic, while more than 90° means hydrophobic. This membrane is hydrophilic with 67.9° of contact angle. Hence, the membrane can facilitate water transport and rejecting other hydrophobic matters.

Based on surface pore (Figure 3), the membrane is in ultra-filtration (UF) which is the most used in water treatment especially in PW treatment [18]. UF membrane has been specialized to remove color, odor, viruses and colloidal organic matter [19,20] also known effectively in oil removal compared to traditional methods in PW treatment [18,21].

Psf membrane is asymmetric, comprising selective layer (up layer) and support layer (bottom layer). The core advantage of this morphology is having strong structure supported by second layer, which can maintain both of high selectivity and high flux.

| Table 2. Membrane Characteristic |
|---------------------------------|
| Items                           | Amount          |
| Contact angle                   | 67.9°           |
| Nominal pore size               | <0.01 µm (UF)   |
| Thickness                       | 0.26 cm         |
| Surface porosity                | 51.2%           |
| Pore morphology                 | Asymmetric      |
| Specification                   | Ultrafiltration |

Hydraulic Membrane Performance

A. Relative permeability

Figure 4 shows the permeability trend over the time for membrane 1 and 2. Those data were obtained under different parameters: using spacer and aeration 1.5 L/min (spacer+bubble), using aeration 1.5
L/min but without spacer (no spacer+bubble) and using neither spacer nor aeration (no spacer+no bubble).

As shown in Figure 4, spacer+bubble system has the highest relative permeability. The no-spacer + bubble system shows better performance than no-spacer + no-bubble system. This finding shows effectiveness of spacer and bubble enhance membrane permeability. Both graphs show about similar of decreasing permeability over time. Permeability decreases rapidly within first 40 min operation and gradually reach plateau for the last 30 min. Sharp decline on permeability on the first 40 min is due to high initial flux (low initial membrane mass transfer resistance) [22,23]. Overtime, membrane mass transfer resistance increases due to pore clogging, cake layer formation, concentration polarization, etc [23,24]. All of them contribute on membrane fouling. Lastly, permeability reaches steady value due to balance between convective flow of foulant approaching membrane surface and its back diffusive flow away from the membrane surface.

B. Effect of air bubble (aeration)
The effect of air bubble in membrane filtration, can be seen by comparing the permeability profile of variable different set-ups: no-spacer+bubble and no-spacer+no-bubble in Figure 4. Both filtration systems operated under air bubbling show higher permeability than no-bubble operation. This suggests that air bubbles can maintain membrane permeability due to their roles in removing foulant from membrane surface. Moreover, air bubbles can help to lift the oil droplets like ones normally seen in dissolved air flotation process. The bubbles have buoyancy force to float those particulates and bring them onto feed liquid surface.

The role of air bubble flotation in waste water treatment has long been known and this phenomenon is utilized in dissolved air flotation (DAF) process. DAF removes dissolved and dispersed oil from produced water, hence can reduce oil and turbidity [25,26]. However, stand-alone DAF is still constricted by the higher energy consumption of generating micro-size bubbles. Employing air bubble in membrane filtration, on another hand, not only gives significant impact to reduce fouling propensity. 

C. Effect of Spacer
The effectiveness spacer in membrane filtration can be seen by the relative value of permeability between spacer+bubble and no-spacer+bubble. Significantly higher permeability was found for spacer+bubble than no-spacer+bubble. This result suggests the role of spacer to maximize the air bubbles contact toward membrane surfaces. Better bubble and membrane contacts leads to get better fouling control.

It is still not clear enough to see the bubble pathway encouraged by spacer. Roughly, Figure 4 shows that the bubble distribution tends to membrane 2, implied by higher permeability and significant improvement. We can conclude that the use of spacer in membrane module is to get excellent bubble distribution.
D. Oil Rejection

To get more precise TOG analyzing, each variable has done by three times measurement (Table 3). The amount of oil rejection can be sequenced from the worse to the best one: no-spacer+no-bubble, no-spacer+bubble and spacer+bubble.

Combination of spacer+bubble gives the best performance in oil rejection due to the role of spacer to maximize the bubble reducing the fouling. Membrane 1 can obtain more than 60% of oil rejection while membrane 2 rejects 55% oil. Meanwhile, combination of no-spacer+bubble doesn’t perform oil rejection as much as spacer+bubble due to the uncertain bubble distribution in term of the spacer absence. On the other hand, it still performs better rejection compared to no-spacer+no-bubble.

Table 3. Oil Rejection

| Variable                  | TOG (mg/L) | %rejection |
|---------------------------|------------|------------|
| M1 | M2 | M1 | M2 |
| No spacer + no bubble     | 7.2        | 8.9        | 35.82 | 21.03 |
| average                   | 7.23       | 8.9        |
| No spacer + bubble        | 5.7        | 7.9        | 50.01 | 27.83 |
| average                   | 5.63       | 8.13       |
| Spacer + bubble           | 4.3        | 5.3        | 60.96 | 55.04 |
| average                   | 4.4        | 5.1        |

Meanwhile, combination of no-spacer+bubble doesn’t perform oil rejection as much as spacer+bubble due to the uncertain bubble distribution in term of the spacer absence. On the other hand, it still performs better rejection compared to no-spacer+no-bubble.

The combination of spacer+air bubble to suppress fouling proves the significant effect in oil rejection. Better permeance is indicated by higher oil rejection. Moreover, it can be concluded that air bubble can decrease fouling propensity by doing both scouring off the foulant from membrane surface and floating those particulates onto PW liquid surface (DAF). Spacer also gives the significant impact to distribute bubbles.

4. Conclusion

Membrane fabrication using polymer blending of Psf and PEG produces membrane ultrafiltration (UF) which is suitable for PW treatment. Membrane performance over time gets declined permeability due to fouling effect. The using of advanced aeration occupied finned spacer performs better fouling control. It functions by removing those foulants and gives significant impact in permeability profile and oil rejection.

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