Process synthesis and optimization of SiO$_2$/PVDF mixed-matrix membrane for oil-water emulsion separation

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Abstract. In this study, and optimized silicon oxide (SiO$_2$)/polyvinylidene fluoride (PVDF) mixed-matrix membrane formulation was developed using response surface methodology (RSM). SiO$_2$ nanoparticles (NPs) concentration (1-3%), silane solution concentration (1:100-3:100 ratio of silane to ethanol) and duration of silanization process (240-600 s) were identified as the factor in affecting the membrane performance, both permeate flux and rejection. The synthesized membranes were characterized in terms of membrane pore size, porosity, surface roughness, and surface wettability. The optimum SiO$_2$/PVDF mixed-matrix membrane formulation was obtained with 2.9% SiO$_2$ NPs concentration, 2.22:100 ratio of silane to ethanol, with 496 seconds of silanation process duration. The optimum SiO$_2$/PVDF mixed-matrix membrane formulation exhibited an extraordinarily high oil droplets rejection (92.01%) with 27.57 L/m$^2$ h of permeate flux at 1 bar of operating pressure.

1. Introduction

Polymeric membrane could be an advanced technology use for separating oil from oil-water emulsion due to consistency in performance, no addition of chemicals in the process, high separation efficiency, easy to operate, and small footprint. The principle of membrane filtration process is simple where the membrane is act as the barrier prohibiting the oil droplets from penetrating through the membrane matrix while allow water molecules with smaller hydrodynamic particle size to pass through. Basically, the membrane performance (both permeate flux and rejection) is greatly affected by membrane’s surface properties including pore size, porosity, surface wettability, and surface roughness [1]. As such, the factors which affect the membrane’s surface properties should be identified for optimizing the synthesis process of the membrane to achieve the greatest membrane filtration performance.

In this study, central composite design (CCD) - response surface methodology (RSM) approach was used to study the weight percent of silicon oxide (SiO$_2$), concentration of silane solution, and silanation process duration as the factors in optimizing the SiO$_2$/PVDF mixed-matrix membrane synthesis process for oil-water emulsion separation. RSM is a statistical approach which could greatly reduce the time and cost from carrying out large number of experiments [2]. With the application of RSM, an exact quantification SiO$_2$/PVDF mixed-matrix membrane formulation could be developed from this study.
2. Materials and method

2.1. Preparation of oil-water emulsion
50 mg sodium dodecyl sulphate (SDS) was dissolved in 1 L of distilled water and stirred at 1500 rpm for 10 minutes until SDS was completely dissolved. Next, 100 μg of engine oil was added drop by drop with the use of micropipette. The mixture was kept stirring at 1500 rpm for 3 hours. The resulted oil-water emulsion was stored at room temperature.

2.2. Synthesis of SiO$_2$/PVDF mixed-matrix membrane
Membrane polymer solution was prepared by dissolving 18 g PVDF into 82 g DMAc as described in our previous study [3,4]. Next, SiO$_2$ NPs was blended into the membrane polymer solution. The mixture was subjected to constant stirring of 250 rpm at 65 °C for 4 hours to form homogeneous solution. The homogeneous membrane polymer solution was then left overnight with stirring at 40 °C. SiO$_2$/PVDF mixed-matrix membrane was synthesized at nominal thickness of 200 μm and immediate immersed into coagulation bath at room temperature. The synthesized SiO$_2$/PVDF mixed-matrix membrane was further grafted with silane-ethanol mixture at different (Tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane: 2-butanol ratio. Dry SiO$_2$/PVDF mixed-matrix membrane was immersed in silane-ethanol mixture at varied silanization duration. Weight percent of SiO$_2$ NPs, concentration of silane-ethanol mixture (ratio X: 100), and silanization duration were the process parameters for synthesis for SiO$_2$/PVDF mixed-matrix membrane with the aid of CCD-RSM approach. They are indicated by process parameter A, B, and C, respectively. The work range of weight percent of SiO$_2$ NPs (A), concentration of silane-ethanol mixture (B), and silanization duration (C) were 0.32-3.68 wt%, 0.32-3.68: 100, and 117.28-722.72 s, respectively.

2.3. Characterization of SiO$_2$/PVDF mixed-matrix membrane
Membrane surface roughness was measured from the image captured by atomic force microscope (AFM) (NX-10, Park Systems, USA). Whereas, surface wettability of the membrane was indicated by contact angle value measured by droplet shape analyzer (EasyDrop FM40, Krüss, Germany). Membrane pore size and porosity were calculated from gravimetric method and Guerout-Elford-Ferry equation, respectively.

2.4. Membrane performance study
A laboratory dead-end membrane filtration unit was used to study the performance of the synthesized membranes. Membrane performance study was conducted by laying the membrane with effective surface area of 14.6 cm$^2$ on the membrane stainless steel holder and 1 bar of operating pressure was exerted across the membrane matrix. Permeate flux (J) of the membrane was calculated from Eq. (1).

\[
J = \frac{V}{At}
\]

Where V is the permeate volume (L), A is the membrane effective surface area (m$^2$), and t is the time taken to collect the permeate (h).

Oil-water emulsion prepared from Section 2.1 was used as the feed solution for assessing the effectiveness of membrane filtration process. Membrane rejection was evaluated at constant pressure of 1 bar. The concentration of oil-water emulsion as feed solution and the permeate were determined from the measurement of its absorbance using UV-vis spectrophotometer at the wavelength of 120 nm. Membrane rejection (R) was calculated using Eq. (2).

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

Where $C_p$ is the concentration of the permeate (mg/L), and $C_f$ is the concentration of feed solution (mg/L).
3. Materials and method

3.1. Membrane characterization

Table 1 summarized the contact angle, porosity, and pore size of the SiO$_2$/PVDF mixed-matrix membrane formulation developed from Design Expert 6.0.8. Contact angle of the membranes was ranging between 67.2º ± 0.28 to 88.8º ± 0.94. Membrane with contact angle smaller than 90º is categorized as hydrophilic membrane. Theoretically, blending of SiO$_2$ NPs into PDVF membrane matrix was expected to increase the membrane surface wettability, leading to the reduction of membrane contact angle [5]. However, a contradict result was obtained from this study. Contact angle was increased with the increasing of SiO$_2$ NPs weight percent added into PVDF membrane matrix. This is possibly due to higher surface roughness created by SiO$_2$ NPs deposited on the membrane surface. Water molecules was prohibited from directly in contact with the membrane surface attributed by the air gaps created between the roughness membrane surface [6]. On the other hand, silanation process had changed the membrane surface became hydrophobic. The non-polar silane chain grafted on the membrane surface had reduced the interaction between membrane surface and the water molecules. Therefore, the increasing of silane solution concentration and silanization duration were leading to the increasing of membrane’s contact angle.

| Membrane | Weight percent of SiO$_2$ NPs | Concentration of silane solution (ratio X:100) | Silanization duration (s) | Contact angle (º) | Porosity (%) | Pore size (nm) |
|----------|-------------------------------|-----------------------------------------------|---------------------------|------------------|--------------|--------------|
| M1       | 1.00                          | 3.00                                          | 240.00                    | 68.2 ± 0.80      | 68.31± 3.19  | 630.037      |
| M2       | 1.00                          | 3.00                                          | 600.00                    | 72.6 ± 3.61      | 77.73±2.29   | 122.567      |
| M3       | 2.00                          | 2.00                                          | 420.00                    | 72.3 ± 3.24      | 76.52±2.83   | 389.516      |
| M4       | 1.00                          | 1.00                                          | 600.00                    | 72.3 ± 3.24      | 76.52±2.83   | 389.516      |
| M5       | 2.00                          | 0.32                                          | 420.00                    | 67.2 ± 0.28      | 65.89±6.49   | 347.360      |
| M6       | 2.00                          | 2.00                                          | 420.00                    | 71.8 ± 0.61      | 80.27±5.85   | 353.269      |
| M7       | 2.00                          | 2.00                                          | 722.72                    | 81.4 ± 2.37      | 69.28±2.30   | 213.704      |
| M8       | 2.00                          | 3.68                                          | 420.00                    | 68.1 ± 0.62      | 67.74±2.66   | 307.636      |
| M9       | 2.00                          | 2.00                                          | 420.00                    | 77.2 ± 0.62      | 73.11±2.25   | 454.860      |
| M10      | 2.00                          | 2.00                                          | 420.00                    | 84.9 ± 0.41      | 76.48±4.89   | 270.419      |
| M11      | 2.00                          | 2.00                                          | 117.28                    | 74.5 ± 7.85      | 73.51±1.56   | 703.120      |
| M12      | 2.00                          | 2.00                                          | 420.00                    | 77.6 ± 1.89      | 70.66±6.12   | 296.680      |
| M13      | 3.00                          | 3.00                                          | 240.00                    | 74.9 ± 0.78      | 69.85±1.89   | 343.160      |
| M14      | 3.00                          | 3.00                                          | 600.00                    | 88.8 ± 0.94      | 79.98±4.48   | 435.537      |
| M15      | 1.00                          | 1.00                                          | 240.00                    | 68.2 ± 1.28      | 69.89±6.41   | 255.373      |
| M16      | 3.68                          | 2.00                                          | 420.00                    | 72.2 ± 0.11      | 74.60±4.25   | 280.700      |
| M17      | 2.00                          | 2.00                                          | 420.00                    | 84.9 ± 1.43      | 75.82±4.39   | 481.321      |
| M18      | 3.00                          | 1.00                                          | 600.00                    | 80.6 ± 0.58      | 78.69±5.54   | 912.262      |
| M19      | 0.32                          | 2.00                                          | 420.00                    | 76.4 ± 1.43      | 72.08±3.31   | 462.710      |
| M20      | 3.00                          | 1.00                                          | 240.00                    | 71.5 ± 0.78      | 70.25±5.77   | 607.617      |

Similarly, membrane porosity and pore size were increased due to the increasing of SiO$_2$ NPs weight percentage, the concentration of silane solution into PVDF membrane matrix, and the prolong of silanization duration. The addition of NPs or grafting of silane onto membrane matrix had interrupt the solvent-non-solvent exchange rate during phase inversion process. Fast solvent and non-solvent exchange rate due to the addition of hydrophilic SiO$_2$ NPs and the hydrophilic-hydrophobic interaction...
between PVDF polymer and silane were contributing to higher porosity and larger membrane pore size [1].

3.2. Membrane performance study

Table 2 summarized the response of SiO$_2$/PVDF mixed-matrix membrane formulation developed from Design Expert 6.0.8. An ideal membrane is the one with high permeate flux and high rejection. Membrane permeate flux is always correlated with membrane surface wettability, membrane porosity, and membrane pore size. Among all membrane formulation, M11 membrane with large membrane pore size, low contact angle, and high porosity was having the greatest permeate flux. However, high permeate flux was always compensated with low rejection as large membrane pore size was not able to retain small solute particles in feed solution. The statement was proven with only 40.90% of rejection was obtained by M11 membrane in oil-water emulsion filtration process. On the contrary, although M2 membrane has the lowest permeate flux due to lower membrane surface wettability, low porosity, and smaller membrane pore size, it does present great rejection towards oil molecules from oil-water emulsion.

Table 2. Response for each membrane formulation developed from Design Expert 6.0.8.

| Membrane | Weight percent of SiO$_2$ NPs | Concentration of silane solution (ratio X:100) | Silanization duration (s) | Permeate flux (L/m$^2$ h) | Rejection (%) |
|----------|-----------------------------|--------------------------------------------|---------------------------|---------------------------|---------------|
| M1       | 1.00                        | 3.00                                      | 240.00                    | 2.553                     | 78.525        |
| M2       | 1.00                        | 3.00                                      | 600.00                    | 1.698                     | 86.912        |
| M3       | 2.00                        | 2.00                                      | 420.00                    | 6.195                     | 93.865        |
| M4       | 1.00                        | 1.00                                      | 600.00                    | 36.025                    | 66.548        |
| M5       | 2.00                        | 0.32                                      | 420.00                    | 4.821                     | 77.505        |
| M6       | 2.00                        | 2.00                                      | 420.00                    | 4.281                     | 92.842        |
| M7       | 2.00                        | 2.00                                      | 722.72                    | 16.298                    | 90.184        |
| M8       | 2.00                        | 3.68                                      | 420.00                    | 4.293                     | 77.505        |
| M9       | 2.00                        | 2.00                                      | 420.00                    | 7.299                     | 86.503        |
| M10      | 2.00                        | 2.00                                      | 420.00                    | 11.759                    | 92.229        |
| M11      | 2.00                        | 2.00                                      | 117.28                    | 56.237                    | 40.899        |
| M12      | 2.00                        | 2.00                                      | 420.00                    | 16.433                    | 95.705        |
| M13      | 3.00                        | 3.00                                      | 240.00                    | 18.301                    | 92.733        |
| M14      | 3.00                        | 3.00                                      | 600.00                    | 10.493                    | 85.714        |
| M15      | 1.00                        | 1.00                                      | 240.00                    | 6.180                     | 90.697        |
| M16      | 3.68                        | 2.00                                      | 420.00                    | 8.086                     | 89.154        |
| M17      | 2.00                        | 2.00                                      | 420.00                    | 8.611                     | 95.296        |
| M18      | 3.00                        | 1.00                                      | 600.00                    | 15.532                    | 90.322        |
| M19      | 0.32                        | 2.00                                      | 420.00                    | 5.305                     | 88.548        |
| M20      | 3.00                        | 1.00                                      | 240.00                    | 8.184                     | 88.548        |

Table 3 and Table 4 shows the ANOVA quadratic model for both membranes permeate flux and membrane rejection. Exponent of silanization time ($C^2$) is the most significant corresponding factor both quadratic models for membrane permeate flux and membrane rejection with the smallest probability > F value [7]. Unfortunately, both developed quadratic models’ probability > F values are greater than 0.05, indicated that the developed quadratic model is insignificant in presenting the relationship between the process variables and responses [8].
Table 3. ANOVA quadratic model for membrane permeate flux.

| Response | Model terms | Sum of squares | Mean square | F value | Probability > F |
|----------|-------------|----------------|-------------|---------|-----------------|
| Quadratic model | 2148.80 | 238.76 | 2.3500 | 0.0997 |
| A | 8.43 | 0.08 | 0.7792 | 0.7792 |
| B | 83.48 | 0.82 | 0.3860 | 0.3860 |
| C | 109.32 | 1.08 | 0.3240 | 0.3240 |
| A² | 40.06 | 0.39 | 0.5441 | 0.5441 |
| B² | 84.64 | 0.83 | 0.3829 | 0.3829 |
| C² | 1112.94 | 10.95 | 0.0079 | 0.0079 |
| AB | 231.48 | 2.28 | 0.1621 | 0.1621 |
| AC | 108.41 | 1.07 | 0.3259 | 0.3259 |
| BC | 262.85 | 2.59 | 0.1388 | 0.1388 |
| Residual | 1016.01 | 101.60 | | |
| Lack of fit | 920.02 | 184.00 | 9.5800 | 0.0134 |
| Pure error | 95.99 | 19.20 | | |
| Cor total | 3164.81 | | | |

Table 4. ANOVA quadratic model for membrane rejection.

| Response | Model terms | Sum of squares | Mean square | F value | Probability > F |
|----------|-------------|----------------|-------------|---------|-----------------|
| Quadratic model | 1565.76 | 173.97 | 1.1800 | 0.3959 |
| A | 93.09 | 93.09 | 0.6300 | 0.4447 |
| B | 78.93 | 78.93 | 0.5400 | 0.4806 |
| C | 280.37 | 280.37 | 1.9100 | 0.1974 |
| A² | 0.17 | 0.17 | 0.0015 | 0.9736 |
| B² | 31.79 | 31.79 | 0.2200 | 0.6519 |
| C² | 1004.61 | 1004.61 | 6.8300 | 0.0259 |
| AB | 9.28 | 9.28 | 0.0630 | 0.8068 |
| AC | 13.83 | 13.83 | 0.0940 | 0.7654 |
| BC | 70.47 | 70.47 | 0.4800 | 0.5045 |
| Residual | 1470.36 | 147.04 | | |
| Lack of fit | 1414.59 | 282.92 | 25.3700 | 0.0015 |
| Pure error | 55.77 | 11.15 | | |
| Cor total | 3036.12 | | | |

The optimum process variables for synthesized SiO$_2$/PVDF mixed-matrix membrane formulation from CCD-RSM approach are 2.9 wt% of SiO$_2$ NPs, ratio of silane-ethanol mixture at 2.22:100, and silanization duration of 496 s. To affirm the optimum process parameters predicted by CCD, runs with suggested optimum process parameters were conducted according to the membrane formulation summarized in Table 5. Nascent membrane (M21) was used as the control while SiO$_2$ NPs SiO$_2$/PVDF mixed-matrix membrane without silanization (M22) was used to investigate the effect of silanization on membrane performance.

Table 5. Optimum process parameters for SiO$_2$/PVDF mixed-matrix membrane formulation from CCD-RSM approach.

| Membrane | Weight percent of SiO$_2$ NPs | Concentration of silane solution (ratio X:100) | Silanization duration (s) |
|----------|-------------------------------|---------------------------------------------|--------------------------|
| M21      | 0                             | 0                                           | 0                        |
| M22      | 2.9                           | 0                                           | 0                        |
| M23      | 2.9                           | 2.22                                        | 496                      |
Figure 1. Contact angle of the suggested SiO$_2$/PVDF mixed-matrix membrane formulation.

Figure 2. Surface roughness of the suggested SiO$_2$/PVDF mixed-matrix membrane formulation (a) M21 (b) M22 (c) M23.

Figure 1 and Figure 2 show the contact angle and surface roughness of three suggested SiO$_2$/PVDF mixed-matrix membrane formulation. The addition of SiO$_2$ NPs into PVDF membrane matrix (M22) had increased the membrane surface wettability due to the hydrophilicity of SiO$_2$ NPs which capable in attracting the water molecules to penetrate through the membrane surface. Whereas the silanation process had converted the SiO$_2$/PVDF mixed-matrix membrane surface into non-polar and hydrophobic, proven by the reducing of membrane surface wettability for M23. Beside the membrane
surface wettability, modification of PVDF membrane matrix with SiO$_2$ NPs and silanation grafting process did increased the membrane surface roughness. The quantitative surface roughness of the membrane was increased followed the trend of M21 (89.16 nm) < M22 (99.96 nm) < M23 (110.53 nm). In-homogeneous distribution of SiO$_2$ NPs into the membrane matrix and the off-peak of silane chains are the factors leading to rough membrane surface. This postulation is supported by FESEM micrographs of SiO$_2$/PVDF mixed-matrix membrane surface as presented in Figure 3.

![FESEM Micrographs](image)

**Figure 3.** Surface roughness of the suggested SiO$_2$/PVDF mixed-matrix membrane formulation (a) M21 (b) M22 (c) M23.

Table 6 summarized the membrane characterization and performance response for suggested SiO$_2$/PVDF mixed-matrix membrane formulation. As explain in Section 3.1, membrane porosity and pore size were increased with the increasing of SiO$_2$ NPs weight percentage and the concentration of silane solution into PVDF membrane matrix, attributed by fast solvent and non-solvent exchange rate or the hydrophilic-hydrophobic interaction between PVDF polymer and silane. Justifying the response of three suggested SiO$_2$/PVDF mixed-matrix membrane formulation, M22 and M23 were having the superior performance with high permeate flux and high oil-in water emulsion rejection as compared to nascent membrane (M21).
Table 6. Membrane characterization and performance response for suggested SiO$_2$/PVDF mixed-matrix membrane formulation.

| Membrane | Membrane characterization | Response |
|----------|---------------------------|----------|
|          | Porosity (%) | Pore size (nm) | Permeate flux (L/m$^2$ h) | Rejection (%) |
| M21      | 81.18        | 620.996      | 37.565                  | 73.32        |
| M22      | 84.66        | 709.479      | 42.840                  | 84.50        |
| M23      | 86.14        | 627.461      | 27.574                  | 92.01        |

4. Conclusion

Synthesis process of SiO$_2$/PVDF mixed-matrix membrane was optimized using Design Expert 6.0.8 software in this study. Exponent of silanization time (C$^2$) is the most significant corresponding factor both quadratic models for membrane permeate flux and membrane rejection with the smallest probability > F value. Statistical analysis suggested that the optimum process variables for SiO$_2$/PVDF mixed-matrix membrane formulation from CCD-RSM approach are 2.9 wt% of SiO$_2$ NPs, ratio of silane-ethanol mixture at 2.22:100, and silanization duration of 496 s which could give optimal rejection of oil droplets and high permeability flux.

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