Optimization studies on TFC membrane for Membrane Gas Absorption (MGA) application

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Abstract. A thin film composite (TFC) membrane has been developed by coating polydimethylsiloxane (PDMS) and glutaraldehyde (GH) on a surface porous polyvinylidene fluoride (PVDF) membrane for membrane gas absorption (MGA) application. The optimum conditions for dip coating method were determined using response surface methodology (RSM). A central composite design (CCD) was used to investigate the effects of two independent factors, which PDMS concentrations (wt%) and dipping time (s) of GH on the four specific responses which are CO2 and N2 permeances, selectivity and contact angle (CA) value. The optimum conditions for PDMS concentration and GH dipping time are 10 wt% and 19 s, respectively where 354 GPU for CO2 permeance, 66 GPU for N2 permeance, 5.4 of selectivity and 132° of CA value were obtained. Through atomic force microscopy (AFM) analysis, the result shown the root mean square roughness (Rms) of the TFC membrane was 381 nm and it was double from untreated membrane Rms value. Therefore, the roughness of the surface membrane contributed to the performance of the separation in the process flow such as in MGA application. By coating PDMS, hydrophobicity of the surface membrane was improved as well.

Keywords: TFC Membrane; Dip Coating; PDMS; Response Surface Methodology

1. Introduction

Membrane gas absorption (MGA) is a gas–liquid contacting operation. The main element in the MGA process is a microporous hydrophobic polymeric membrane. The gas stream is fed to one side of the membrane, and at the same time, liquid absorbent flows on the other side of the membrane. The microporous hydrophobic membrane’s serves as a wall to separate the gas phase from the liquid absorbent. The liquid absorbent should have a high attraction for components that must be removed from the gas stream. Meanwhile, these components will diffuse through the gas-filled pore of the membrane from the surface to the other side of the membrane, which is followed by absorption of the component in the liquid absorbent. Basically, absorption in the liquid occurred by physical absorption (e.g., water) [1] or by a chemical reaction (e.g., amine solution) [2]. Therefore, the selectivity of this process is determined by the strength of the liquid absorbents that absorb the component. Even the membrane does not contribute to the selectivity; however, the permeability of the component is dependent on the pores of the membrane. In addition, the membrane also plays an important role in ensuring that the two phases are separated and providing a large contact surface area [3,4]. MGA is also used for the removal of carbon dioxide (CO2), sulphur dioxide (SO2), nitrogen dioxide (NO2) and other nitrogen oxides (NOx), hydrogen sulphide (H2S), ammonia (NH3), tropospheric ozone (O3) and many other different compounds from gas streams, especially those that exist in flue gas, in natural gas, indoors and in off gases [5,6].
The selection of the type of membrane has a significant effect on the MGA process. Because the liquid absorbents are generally aqueous solutions that are used for absorption purposes, wetting problems seem like a major issue for MGA. Using a hydrophobic membrane leads to larger contact angles and thus is efficient in minimising the wetting problem. Polytetrafluoroethylene (PTFE) membrane material has a very low surface energy (19.1 mN/m), and this material has a high resistance to wetting. However, PTFE membranes are very expensive. In contrast, polypropylene (PP) (30.0 mN/m) and polyvinylidene fluoride (PVDF) (30.3 mN/m) membrane materials have a sufficiently low surface energy, are inexpensive and are commercially available with small pore diameters [7,8].

Thin film composite (TFC) technology has been developed for top surface coating supports in the fabrication of reverse osmosis membranes [9]. Many methods of fabricating TFC membranes have been reported in the literature. These include surface grafting, pore-filled grafting and dip coating. The dip-coating process was successfully implemented for membranes before the measurement of gas separation permeance because the silicone rubber was shown to be able to recover the intrinsic permselectivity of the skin layer of an asymmetric membrane [10]. Meanwhile, the separation and flux behaviour may be interpreted in terms of both chemical and structural changes occurring within the composite coating [11]. In the current study, the dip coating was adapted to coat the surface of a microporous PVDF membrane using silicone rubber. We propose an alternative method for decreasing water molecule interactions (increasing the hydrophobicity) using the dip-coating method. The aim of the present study was to determine the effect of the silicone rubber concentration and the dipping time on the cross-linking agent in a PVDF membrane based on CO$_2$ and N$_2$ single permeation, selectivity and contact angle (CA) measurements. To maximise the permeation of CO$_2$, an optimisation process was followed using response surface methodology (RSM) with a central composite design (CCD). The properties of the optimised surface of the TFC membrane were compared with an untreated PVDF membrane.

2. Methods
2.1 Materials
Flat sheets of 0.1 µm-thick PVDF membranes were purchased from Millipore Asia LTD. Polydimethylsiloxane (PDMS), silicone rubber and glutaraldehyde (GH, 25% aqueous solution, cross-linking agent) were procured from Sigma Aldrich (M) Sdn. Bhd. All solvents were used without further purification. The material properties are tabulated in Table 1 and Table 2.

Table 1: Properties of the membranes

| Properties       | 0.1 µm PVDF membrane |
|------------------|----------------------|
| Module:          | Flat Sheet           |
| Diameter:        | 470 mm               |
| Thickness:       | 125 µm               |
| Porosity:        | 70%                  |
| Wettability:     | Hydrophobic          |
Table 2: Properties of the chemicals

| Properties                  | PDMS                   | GH          |
|-----------------------------|------------------------|-------------|
| Molecular formula:          | \((\text{C}_2\text{H}_6\text{OSi})_n\) | \(\text{C}_5\text{H}_8\text{O}_2\) |
| Density:                    | 965 kg/L               | 1.06 g/mL   |
| Melting Point:              | N/A                    | -14 °C      |
| Boiling Point:              | below approximately 200 °C | 187 °C     |
| Molar Mass:                 | N/A                    | 100.12 g/mol|
| Chemical Structure:         | ![Chemical Structure](image) | ![Chemical Structure](image) |
measured by a soap bubble flow meter. Each set of data was determined as an average of three replicates.

The permeance \( (P/l) \) for TFC membranes was calculated using eq. (1) and expressed in GPU (1 GPU = \( 1 \times 10^{-6} \) cm³(STP)/(cm² s cm Hg)).

\[
P \frac{V}{l} = \frac{At\Delta p}{A \Delta p (\text{cm}^3\text{(STP)})/(\text{cm}^2 \text{s cm Hg})}
\]  

(1)

where \( l \) is the thickness of the membrane in cm, \( A \) the effective membrane area in cm², \( V \) is the volume (cm³) displaced in time \( t \) (s) and \( \Delta p \) is the transmembrane pressure expressed in cm Hg. The selectivity \( (\alpha) \) is expressed as the ratio of two pure gas permeabilities, as stated in eq. (2).

\[
\alpha_{ij} = (P/l_i)/(P/l_j)
\]  

(2)

where \( i \) is CO₂ and \( j \) is N₂.

2.4 Contact angle (CA) measurement

In this work, the values of the CA of deionised water on different surface membranes were measured. The measurement was performed on sessile drops with a computerised Optical Contact Angle SCA 15 from Germany. Using the SCA 15, drop volume was controlled with a microsyringe followed by placing the surface near the needle; 6 µl of deionised water was squeezed out of the syringe. The surface was pulled out of the drop. Finally, the contact angles were measured by using the Laplace-Young equation, and the image was captured. The effects of evaporation of the liquids used were minimised by finishing each measurement within a period of less than 1 min. It was found experimentally that the contact angle remained constant within this period. The result of all measurements was the mean of at least 10 single measurements.

2.5 Experimental design and RSM

To design the experimental plan, response surface methodology (RSM) was utilised to optimise the TFC membrane performance, and a full fractional central composite design (CCD) was adopted to fit a second-order model. The design consisted of 13 sets of experiments. The basic theoretical aspects, the fundamentals assumptions and the experimental implications of RSM have been discussed elsewhere (Montgomery, 2001). The second-order model was selected for predicting the optimal point and is expressed as eq. (3).

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2
\]  

(3)

where \( Y \) represents response variable (CO₂ and N₂ single permeation, selectivity and CA), \( \beta_0 \) is the interception coefficient, \( \beta_1 \) and \( \beta_2 \) are linear terms, \( \beta_{11} \) and \( \beta_{22} \) are quadratic terms and \( X_1 \) and \( X_2 \) are the independent variables studied (PDMS concentration and dipping time of GH). The ranges and the levels of the variables investigated in the study are given in Table 4.

Table 4: Experimental range and level of the independent variables
A complete description of the experimental design is shown in Table 5. Panel I in Table 5 represents the level in terms of coded variables, while Panel II shows the conditions used with the original unit measurement.

Table 5: CCD for the study of two experimental variables in coded units

| Run no. | Panel I | Panel II |
|---------|---------|----------|
|         | PDMS concentration, \( A \) (\%w/v) | Dipping time of GH, \( B \) (s) | PDMS concentration, \( A \) (\%w/v) | Dipping time of GH, \( B \) (s) |
| 1       | 1 1 1 | 12 30   |
| 2       | 0 0 0 | 9 20    |
| 3       | -1 1 1 | 6 30    |
| 4       | -1.682 0 1 | 5 20    |
| 5       | 0 0 0 | 9 20    |
| 6       | 0 0 0 | 9 20    |
| 7       | 1 -1 1 | 12 10   |
| 8       | 0 -1 1 | 9 10    |
| 9       | 0 -1.682 1 | 9 6    |
| 10      | 1.682 0 1 | 13 20   |
| 11      | -1 -1 1 | 6 10    |
| 12      | 0 0 0 | 9 20    |
| 13      | 0 1.682 0 | 9 34    |

Regression analysis was performed by Design Expert v.6.0.7 (Stat- Ease Inc. Minneapolis). Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The quality of the fit polynomial model was expressed by the coefficient of determination \( R^2 \), and its statistical significance was checked by the Fisher \( F \)-test in the same program. Model terms were selected or rejected based on the \( P \) value (probability) with a 95% confidence level. Three-dimensional plots and their respective contour plots were obtained based on the effects of the levels of two variables. From these three-dimensional plots, the simultaneous interaction of two factors on the responses was studied.

3. Results and discussion

3.1 Experimental results
Experiments were conducted based on the design in Table 5, and the relevant results are shown in Table 6, which lists the CO\(_2\) and N\(_2\) single permeation, the selectivity and the CA value.

Table 6: Experimental results

| Run no. | CO\(_2\) permeance cm\(^3\) (STP)/cm\(^2\).s.cm Hg | N\(_2\) permeance cm\(^3\) (STP)/cm\(^2\).s.cm Hg | selectivity | CA (°) |
|---------|---------------------------------------------|---------------------------------------------|-------------|--------|
| 1       | 343.11                                      | 132.42                                      | 3.96        | 122.38 |
| 2       | 337.07                                      | 62.02                                       | 5.03        | 132.53 |
| 3       | 157.67                                      | 83.41                                       | 1.35        | 128.87 |
| 4       | 235.33                                      | 82.91                                       | 0.91        | 126.92 |
| 5       | 339.01                                      | 61.21                                       | 5.31        | 132.42 |
| 6       | 337.28                                      | 61.73                                       | 5.00        | 132.45 |
| 7       | 390.01                                      | 91.03                                       | 5.31        | 134.75 |
| 8       | 337.30                                      | 60.88                                       | 4.69        | 132.36 |
| 9       | 396.19                                      | 112.54                                      | 7.09        | 143.21 |
| 10      | 405.32                                      | 123.97                                      | 3.88        | 122.72 |
| 11      | 327.44                                      | 142.76                                      | 4.00        | 124.02 |
| 12      | 337.01                                      | 61.06                                       | 5.23        | 132.40 |
| 13      | 216.93                                      | 133.21                                      | 2.79        | 123.05 |

3.2 ANOVA analysis

The results are further analysed using Design Expert Software. The relationship between two controllable variables (PDMS concentration and dipping time of GH) and four important responses (CO\(_2\) and N\(_2\) permeance, selectivity and CA value) for the TFC membrane performance is studied. Model terms that are significant are desired to obtain a good fit in a particular model. A CCFD shown in Table 4 allows the development of mathematical equations in which each response variable \(Y\) is assessed as a function of PDMS concentration \((A)\) and dipping time of GH \((B)\) and calculated as the sum of a constant, two first-order effects (terms in \(A\) and \(B\)), one interaction effect \((AB)\) and two second-order effects \((A^2\) and \(B^2\)), according to Eq. (3). The results obtained are then analysed by ANOVA to assess the “goodness of fit”. Only terms found to be statistically significant are included in the model. The non-significant terms can be reduced by reselecting only the significant terms to be included in the model. The model terms with “Prob > F > 0.5” will be eliminated from the model.

The \(A, B, A^2, B^2\) and \(AB\) model terms are found to be significant for the CO\(_2\) permeance. The \(A^2, B^2\) and \(AB\) model terms are found to be significant for the N\(_2\) permeance, and the \(A, A^2, B^2\) and \(AB\) model terms are found to be significant for the selectivity. Meanwhile, the \(B, A^2\) and \(AB\) model terms are found to be significant for the CA value. These results clearly show that interaction effect between the PDMS concentration and the dipping time of GH plays an important role in generating a high CO\(_2\) permeance and producing a higher CA value. The quadratic model is well fitted to the observed data, and the following empirical models in terms of coded values are obtained for the CO\(_2\) and N\(_2\) permeance, selectivity and CA value, respectively:
1) CO₂ permeance

\[ Y_1 = +337.33 + 55.10A -11.25B -27.83A^2 -54.23B^2 + 4.47AB \]

2) N₂ permeance

\[ Y_2 = +61.49 + 22.42A^2 + 30.35B^2 + 25.18AB \]

3) Selectivity

\[ Y_3 = +5.49 + 0.33A -1.46A^2 -1.77B^2 -0.47AB \]

4) CA value

\[ Y_4 = +132.46 - 4.51B -4.59A^2 - 4.30AB \]

The coefficients with one factor represent the effect of the particular factor, while the coefficients with second-order terms represent the quadratic effect. A positive sign in front of the term indicates a synergistic effect, while a negative sign indicates an antagonistic effect. The statistical parameters obtained from the ANOVA for the reduced model of the responses are given in Table 7.

Table 7: Statistical parameters obtained from the ANOVA for the reduced models

| Variables     | CO₂ permeance | N₂ permeance | Selectivity | Contact angle |
|---------------|---------------|--------------|-------------|---------------|
| Significant terms | A,B,A²,B²,AB  | A²,B²,AB     | A,A²,B²,AB  | B,A²,AB       |
| \( R^2 \)     | 0.9997        | 0.9347       | 0.9868      | 0.8358        |
| \( R^2 \) adjusted | 0.9994        | 0.8879       | 0.9773      | 0.7185        |
| \( \text{Prob} > F \) | <0.0001       | 0.0005       | <0.0001     | 0.0013        |
| Adequate precision | 176.495      | 11.897       | 22.646      | 9.247         |
| Standard deviation, SD | 1.48         | 10.67        | 0.25        | 3.18          |
| Coefficient of variance, | 0.51         | 11.47        | 7.05        | 2.45          |
| CV            |               |              |             |               |
| Probability of lack of fit | 0.32        | 0.01         | 0.07        | 0.01          |

The ANOVA results of the quadratic models with \( \text{Prob} > F < 0.05 \) for all the responses presented in Table 7 indicate that the model equation adequately describes the response surfaces of CO₂ permeance, N₂ permeance, selectivity and CA value in the interval of the investigation. The effect of each variable on the response is a combination of the coefficients and the variable values, as well as a joint effect of the variables that cannot be observed by conventional experimental methods. The high \( R^2 \) value, close to 1, is desirable, and the predicted \( R^2 \) must be in reasonable agreement with the adjusted \( R^2 \) for a significant model (Nordin et al., 2004). The values of \( R^2 \) for CO₂ permeance, N₂ permeance and selectivity and CA value are 0.9997, 0.9347, 0.9868 and 0.8358, respectively. In this case, these values indicate that only 0.03–16.42% of the total variation is not explained by the model. The values of the adjusted \( R^2 \) of 0.9994, 0.8879, 0.9773 and 0.7185, respectively, for CO₂ permeance, N₂ permeance selectivity and CA value, are also high to support the high significance of the model [12]. The CV, the ratio of the standard error of the estimate to the
mean value of the observed response (as a percentage), is a measure of the reproducibility of the model. As a general rule, a model is reasonably reproducible if its CV is not greater than 10%. The CV values obtained for all responses studied in Table 7 are below 10%, except the value for N$_2$ permeance. This result is reasonable because the goal of this research is to obtain a high permeability of CO$_2$ instead of N$_2$, which is more important for controlling the structure of the PVDF membrane for high selectivity and CA values.

It is important to check the fitted model to ensure that it provides an adequate approximation to the real system. Fig. 2 shows a comparison of the actual values of the respective responses that were obtained from the experiments and the estimation values from the regression model. As observed in Fig. 2, points above the diagonal line were those overestimated and vice versa. All four graphs shown in Fig. 2 generally indicate that all experiment design points were distributed along the diagonal line. This shows that the models are adequate for predicting the CO$_2$ permeance, N$_2$ permeance, selectivity and CA value within the range of the variables studied.
Fig. 2: Design-expert plot. Predicted vs. Actual plot for: (a) CO$_2$ permeance, (b) N$_2$ permeance, (c) selectivity and (d) contact angle.
3.3 Analysis of the response surface

The response surface plot for CO$_2$ permeance is shown in Fig. 3(a). The figure shows the effect of the concentration of PDMS on the CO$_2$ permeance at the various dipping times for 20\% wt of GH as a cross-linking agent. From the figure, a peak suggests that the optimum condition for maximum CO$_2$ permeance is well inside the design boundary. There is a clear elongated hill running along the time in glutaraldehyde axis on the plot of the three-dimensional response surface of the quadratic model for the CO$_2$ permeance. As can be observed in Fig. 3(a), the maximum CO$_2$ permeance is achieved at a concentration of PDMS of 10 -11 wt% and between 15- 20 s of GH dipping time. For further increases in the concentration of PDMS and the GH dipping time beyond the optimum condition, the CO$_2$ permeance will decrease.

Fig. 3(b) shows the response surface for N$_2$ permeance. The figure indicates that the N$_2$ permeance significantly decreases with the PDMS concentration and time of GH dipping. In the same range, 10 -11 wt\% of PDMS concentration and between 15- 20 s of GH dipping time, the lowest peak of N$_2$ permeance is achieved. Fig. 3(c) shows the response surface for CO$_2$/N$_2$ selectivity. As can be observed in Fig. 3(c), the maximum peak of selectivity is very clear at the concentration of PDMS of 10 -11 wt\% and between 15- 20 s of GH dipping time.

From Fig. 3(a-c), we also found that the defects on the surface of the skin layer of the membranes were completely sealed with PDMS silicone rubber film. Silicone rubber was proven to be able to recover the intrinsic permselectivity of the skin layer of an asymmetric membrane [13]. In addition, the CO$_2$ permeance decrease after the optimum region is due to a decrease in the surface porosity of the composite membrane by the PDMS layer. In contrast, the GH as a cross-linking agent may contribute to the existence of resistances in the substructure and the inner skin layer of the membranes. Therefore, the membrane pores became smaller and only allowed CO$_2$ to pass through rather than N$_2$. Therefore, the influence of these resistances is more significant to CO$_2$ permeance and CO$_2$/N$_2$ selectivity, respectively. However, according to Shieh et al., if multilayers of silicone rubber were applied on membrane surfaces, there would be a decrease in gas permeance because this leads to a thicker layer of coating. In contrast, the selectivity is significantly improved due to the sealing of defects by the silicone rubber [14]. Because the membrane does not contribute to the selectivity in the MGA process, it is important to produce a membrane with a high permeability towards CO$_2$. Meanwhile, Fig. 3(d) demonstrates the effect of the concentration of DPMS and the dipping time of GH on the CA value of the surface membrane. The hydrophobicity of membranes is represented in terms of the CA between the water and membrane. The CA value is an angle between the liquid and the solid. In the case of water, a material is deemed to be hydrophobic if the contact angle is higher than 90° (Wang et al., 2004). As the concentration of PDMS and the dipping time of GH are increased, the CA also increases. As we can see, the optimum value of CA is approximately 133° at the concentration of PDMS of 7.5- 11 wt\% and between 15- 20 s of GH dipping time. However, Fig. 3(d) also shows that an increased concentration of DPMS and an increased dipping time of GH decrease the CA values. This might be due to the interaction between PDMS and glutaraldehyde past the optimum conditions, contributing to an incomplete seal on the surface of the membrane. The consequences would involve the creation of pores that were not hydrophobic enough, resulting in a decline of the CA values.
Fig. 3: Design-expert plot. Response surface plot for (a) CO$_2$ permeance, (b) N$_2$ permeance, (c) selectivity and (d) CA value.
3.4 Optimisation analysis

Numerical optimisation was used to generate the optimal conditions for the targeted responses. Optimisation finds a set of operating conditions that either optimises all of the responses or at least keeps them within the desired range. In this model, the responses for CO$_2$ permeance, selectivity and CA value were required to be maximised. However, the N$_2$ permeance value was set in a range. All the criteria for the optimisation analysis are tabulated in Table 8. Design Expert software was used to obtain the optimal conditions for all factors.

Table 8: Model validation

| Factors               | Goal          | Value  |
|-----------------------|---------------|--------|
| Variables             |               |        |
| PDMS concentration    | is in range   | 10     |
| Time for glutaraldehyde | is in range | 19     |
| Responses             |               |        |
| CO$_2$ permeance      | maximise      | 360.32 |
| Predicted             | 354.83        |        |
| Experimental          | 342.76        |        |
| N$_2$ permeance       | is in range   |        |
| Predicted             | 66.69         |        |
| Experimental          | 65.66         |        |
| Selectivity           | maximise      | 5.54   |
| Predicted             | 5.41          |        |
| Experimental          | 5.22          |        |
| CA value              | maximise      | 143.21 |
| Predicted             | 132.29        |        |
| Experimental          | 130.21        |        |

As mentioned in Table 8, the level of variables optimising the predicted response was 10 wt% of PDMS and 19 s of GH dipping time. Under these conditions, the predicted CO$_2$ and N$_2$ permeance was 354.83 GPU and 66.69 GPU, respectively. Meanwhile, the predicted selectivity and CA value was 5.41 and 132.29°, respectively. Using these conditions, a verification experiment was performed. The experimental values were close to the predicted values from the model. Small errors existed between the predicted and experimental values, which were 3.4%, 1.54%, 3.51% and 1.57%, respectively, for CO$_2$ permeance, N$_2$ permeance, selectivity and CA value.

After the optimisation was performed, the properties of the optimised surface of the TFC membrane were compared with those of an untreated PVDF membrane. The root mean
square roughness ($R_{\text{ms}}$) and maximum and minimum elevations recorded for the optimised TFC membrane and an untreated PVDF membrane are shown in Table 9.

Table 9 shows that the TFC membrane surface has a roughness which is significantly higher than that of an untreated PVDF membrane surface.

Table 9: The comparison properties

| Membrane       | CA value | $R_{\text{ms}}$ (nm) | Maximum elevation (nm) | Minimum elevation (nm) |
|----------------|----------|-----------------------|------------------------|------------------------|
| Optimised TFC membrane | 130.21   | 381                   | 1277                   | -1141                  |
| Untreated PVDF membrane     | 122.17   | 197                   | 746                    | -840                   |

Atomic force microscopy (AFM) was used to show the roughness of both membranes, as shown in Fig. 4. The figure shows the lumpy aggregates were observed from the AFM image. The lumpy aggregates protrude out of the surface and can be observed as bright high peaks, while the pores are depressed into the surface and can be observed as dark regions. Despite this result, the optimised conditions of the TFC membrane provided the maximum CO$_2$ permeance, selectivity and CA value. The AFM analysis revealed that roughness contributes to the hydrophobicity of the TFC membrane. This membrane will be suitable for use in process flow separation for processes such as the MGA process.

4. Conclusions

Optimisation of the dip coating of PVDF membranes with respect to CO$_2$ and N$_2$ permeances, selectivity and CA values has been investigated. Response surface methodology using CCD was applied to determine the optimum conditions for obtaining the maximum CO$_2$ permeance, selectivity and CA value and the lowest N$_2$ permeance. The optimum conditions for PDMS concentration and glutaraldehyde dip coating time are 10 wt% and 19 s, respectively, where 354 GPU for CO$_2$ permeance, 66 GPU for N$_2$ permeance, a selectivity of 5.4 and a CA value of 132° can be obtained. The dip coating was also used to create a hydrophobic surface through surface roughness. This is proved by the $R_{\text{ms}}$ values, which are 381 nm and 197 nm for the TFC membrane and an untreated PVDF membrane, respectively.
Fig. 4: AFM images: (a) three-dimensional optimised TFC membrane, (b) three-dimensional untreated PVDF membrane, (c) top surface of the optimised TFC membrane and (d) top surface of the untreated PVDF membrane

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