Journal of Physical Science, Vol. 35(2), 19–32, 2024

PP/PVDF Hollow Fiber Membrane Coatings for CO_2 Capture: Interaction Parameters via Box-Behnken Design

Abdul Latif Ahmad,* Mohd Hazarel Zairy Mohd Harun, Muhammad Aiman Kelana Putra, Amir Ikmal Hassan and Muhd Izzudin Fikry Zainuddin

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
14300 Nibong Tebal, Pulau Pinang, Malaysia

*Corresponding author: chlatif@usm.my

To cite this article: Ahmad, A. L. et. al. (2024). PP/PVDF hollow fiber membrane coatings for CO_2 capture: Interaction parameters via Box-Behnken Design. *J. Phys. Sci.*, 35(2), 19–32. https://doi.org/10.21315/jps2024.35.2.2

To link to this article: https://doi.org/10.21315/jps2024.35.2.2

ABSTRACT: *Polyvinylidene fluoride (PVDF) membrane has shown potential for CO_2 capture due to their chemical stability and mechanical strength. The coating process using polypropylene (PP) influenced the CO_2 flux. This study optimises the coating parameters on the PVDF membrane using Box-Behnken Design (BBD). Key factors examined were methyl ethyl ketone (MEK) concentration, operating time and coating cycles. The investigated PVDF membrane was employed in the membrane gas adsorption (MGA) to examine the CO_2 flux. Experimental data were fitted to a second-order polynomial quadratic model, yielding an R^2 value of 0.9028, indicating a strong fit. The optimisation revealed that 25% MEK concentration, 30 min of operating time and single coating cycle obtained the highest desirability score of 0.945. Significant factors include the MEK concentration (p-value of 0.0228), operating time (p-value of 0.0018) and coating cycles (p-value of 0.0164). This model effectively captures the linear and interaction effects of the variable on the CO_2 flux. The optimised parameters significantly enhance the CO_2 flux, contributing to the development of a high-performance membrane for CO_2 capture. The application of the optimised PVDF membrane in MGA system demonstrates its efficiency in CO_2 separation. This study advances membrane technology, providing a robust framework for future research in CO_2 separation.*

Keywords: CO_2 capture, PVDF membrane, coating parameters, interaction parameter, Box-Behnken Design

1. INTRODUCTION

The ever-increasing levels of carbon dioxide (CO_2) emission have raised significant concerns on global climate change. Efficient CO_2 capture and separation technologies are crucial to mitigate these environmental issues. Membrane technology has emerged as a promising solution owing to its energy efficiency, operational simplicity, tunable formulation and scalability.[1,2] Among various membrane materials, polyvinylidene fluoride (PVDF) has shown considerable potential for CO_2 capture due to their chemical stability, mechanical strength and processability.[3,4] The performance of PVDF membranes in CO_2 capture can be significantly influenced by the membrane fabrication process particularly involved in the coating process.[5,6]

The coating process is crucial in determining the structure and properties of PVDF membranes, directly impacting their effectiveness in gas separation applications. Coating involves forming a thin, uniform film on substrate. The quality of this film is crucial to achieve desirable membrane characteristics. Polypropylene (PP) was found to be an excellent coating agent due to its chemical resistance and hydrophobic properties. Several studies found that PP dissolved in non-solvent such as methyl ethyl ketone (MEK) resulted on homogenous solution, forming a uniform coating mixture and enhance the hydrophobic properties of the membrane.[7,8] On the other hand, coating parameters such as concentration of coating solution, duration of coating process and number of coating cycles play vital roles in defining membrane morphology, flux and selectivity. Finding the interaction of these parameters is essential to enhance the performance of PVDF membrane for CO_2 separation.

The primary aim of optimising coating parameters is to improve the hydrophobicity of PVDF membrane, which is essential for enhancing CO_2 in membrane gas adsorption (MGA). To systematically explore the effect of coating parameters and their interaction on CO_2 flux, Box-Behnken Design (BBD), a robust statistical tool for response surface methodology (RSM). Among various RSM techniques, the BBD stands out due to its efficiency and reduced number of experimental runs required compared to Central Composite Design (CCD) or Full Factorial Design (FFD).[9–11] BBD allows for the exploration of quadratic relationships without the need for a large number of experimental trials, making it cost-effective and time efficient. By leveraging the BBD, this study aims to identify the optimal coating parameters that maximise the CO_2 flux of PVDF membranes. The findings from the current work are expected to contribute significantly to the development of high-performance membranes for CO_2 capture and separation offering viable solutions to address the pressing issue of CO_2 emissions.

2. METHODOLOGY

2.1 Materials

Commercial PP (Sigma Aldrich, Darmstadt, Germany, > 99% purity) was used as a coating solution. A commercial hollow fiber, PVDF (MSFUF1040) obtained from IT Tech Research, Malaysia was used a support for coating solution. MEK (> 99.55 purity, Merck) is a non-solvent and act as additive to enhance the surface hydrophobicity of the PVDF. Xylene (purity > 99%) obtained from Merck, Germany was used as polymer solvent to dissolve commercial PP. Industrial grade CO_2 (purity > 99%) was employed throughout the MGA process. Distilled water and 0.001M sodium hydroxide (NaOH) (> 99% purity) was used for the measurement of CO_2.

2.2 Experimental

The experimental procedure was followed to the method in the previous published work.[7] The hydrophobic coating solution was prepared in the beaker and poured into a 250 mL measuring cylinder. PVDF hollow fiber was sealed with epoxy to prevent coating solution entering the membrane. The PVDF hollow fiber membrane was initially dipped into the MEK followed by immersion in the dissolved PP. Subsequently, the sample was cured under vacuum at a constant temperature range (40°C–50°C) for 3 h. The modified PVDF membrane was placed in the module for the MGA process to measure the flux of CO_2. The process conducted was in the countercurrent mode where the gas flowed in the lumen side (120 mL/min) meanwhile liquid phase flowed (100 mL/min) in the shell side. The flowrate of liquid phase made up by distilled water was measured using a flowmeter. All the experiments were conducted at room temperature. Figure 1 shows the schematic illustration of the coating experiment and MGA process. The CO_2 flux (mol/m^2.s) was measured using Equation (1) and Equation (2) as described by Hassan et al.[7]

$$\mathrm{J}_{\mathrm{CO}_2} = \frac{Q_{l_n} \times C}{A} \tag{1}$$

$$C = \frac{MW_{\mathrm{CO}_2} \times \text{NaOH molarity} \times \text{Volume of NaOH titrated } (L)}{\text{Volume of distilled water sample } (L)} \tag{2}$$

Where Q_{l_n} is the flowrate of distilled water (m^3/s), C is CO_2 concentration (mol/m^3), A is effective are of membrane module (m^2) and MW_{CO_2} is molecular weight of CO_2.

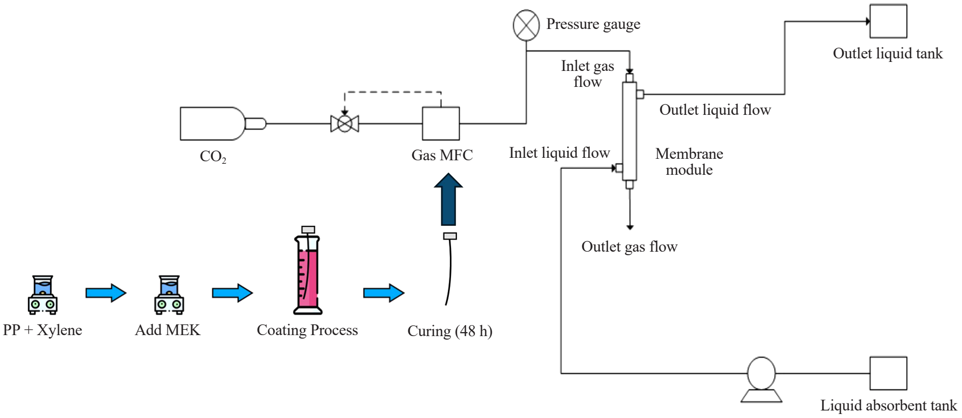

Figure 1: Schematic illustration of coating and MGA process.

2.3 Box-Behnken Design

BBD was employed using Design Experts 13. The key parameters were selected for optimisation was MEK concentration, operating time and coating cycles. These parameters were chosen based on their significant influence on the membrane morphology and CO_2 flux. The MEK concentration effects the dissolution and distribution on coating material (PP), the operating time determines the interaction duration between PVDF and coating solution. The number of coating cycles impacts the uniformity and thickness of coating layer. Table 1 shows the design matrix for the selected parameters.

Table 1: Experimental conditions for BBD

Run	MEK concentration (mg/L)	Operating time (min)	Coating cycles
1	25	30	1
2	25	30	3
3	40	60	1
4	25	60	2
5	25	90	3
6	25	60	2
7	25	60	2
8	25	90	1
9	10	30	2
10	40	90	2
11	10	60	1

(*Continued on next page*)

Table 1 (*Continued*)

Run	MEK concentration (mg/L)	Operating time (min)	Coating cycles
12	40	60	3
13	10	60	3
14	25	60	2
15	40	30	2
16	10	90	2
17	25	60	2

The experimental data obtained from the BBD were analysed using statistical software to develop a response surface model. This model was used to identify the optimal conditions for maximising CO_2 flux. The adequacy of the model was evaluated using analysis of variance (ANOVA) and the significance of model terms was determined.

3. RESULTS AND DISCUSSION

3.1 Effect of MEK Concentration

Figure 2 shows the effect of MEK concentration of CO_2 flux. It is evident that CO_2 flux varies significantly with changes in MEK concentration. Initially, as MEK concentration increases, CO_2 flux rises, reaching an optimum point before declining at higher concentration. The initial increases are attributed to the enhanced dissolution and uniformity of the PP coating solution. MEK effectively disperses the PP facilitating a more homogenous and thin coating layer on the PVDF membrane. However, beyond a certain MEK concentration, the CO_2 flux decreases. This phenomenon may be due to the excessive solvent presence, leading to overly dense or thick coatings that hinder gas diffusion.[12] High MEK concentrations can cause aggregations of the PP molecules, creating a more compact and less porous layer that restricts CO_2 pathway.[13]

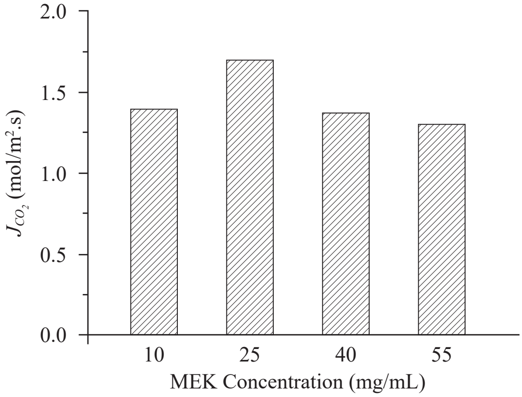

Figure 2: Effect of MEK concentration on the CO_2 flux.
Note: Operating time = 30 min; Coating Cycle = 1

3.2 Effect of Operating Time

Operating time is varied to determine the effect on the CO_2 flux of PVDF membrane, as illustrated in Figure 3. As the operating time increases, the flux decreases. This trend suggests that optimal interaction between PVDF and the coating solution occurs within a specific time frame. As the operating time extends, the PVDF surface becomes formed excessive dense layer caused by overcoating.[14] Overcoating causes the membrane pores to become narrowed and blocked, hindering CO_2 diffusion through the membrane.[15] Therefore, identifying and maintaining optimal operating time is crucial for achieving high CO_2 flux. The findings align with the theoretical understanding that excessive exposure to coating solution can deteriorate membrane performance by compromising pore structure and increase resistance to gas flow.

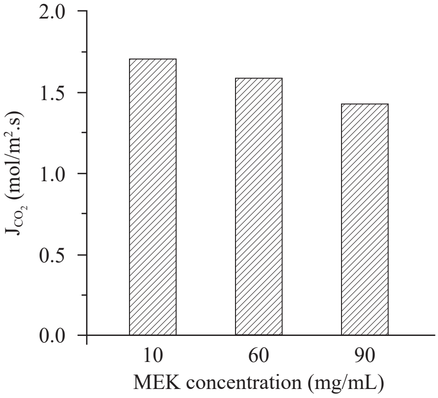

Figure 3: Effect of operating time on CO_2 flux.
Note: MEK concentration = 25 mg/L; Coating Cycle=1

3.3 Effect of Coating Cycles

Figure 4 illustrated the relationship between number of coating cycles and CO_2 flux in PVDF membrane. As the number of coating cycles increases, a clear decrease in CO_2 flux is observed. This trend can be attributed to the accumulation of PP layer on the membrane surface. With each additional coating cycle, the thickness of the coating layer increases, which can lead to several issues that negatively impact the flux.[16] The first coating cycle helps in forming a uniform and defect-free coating, enhancing selective layer that facilitates CO_2 transport. However, as the coating cycles increase, the coating layer becomes excessively thick, creating a dense layer. Excessive coating thickness led to the blockage of pores. The dense layers formed after multiple cycles can obstruct the gas pathways, increasing the transport resistance thus lowering flux.

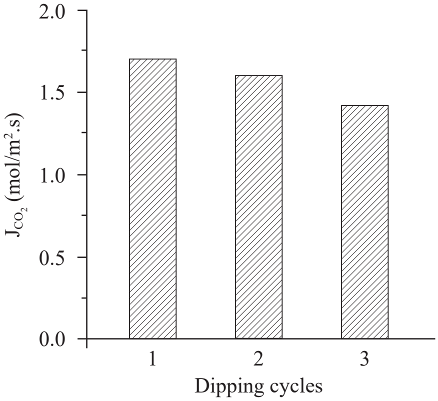

Figure 4: Effect of coating cycle on CO_2 flux.
Note: MEK concentration = 25 mg/L; Operating time = 30 min

3.4 ANOVA

By using BBD, this study investigated the optimisation of coating parameters by evaluating three input parameters; MEK concentration, operating time and coating cycles. The BBD approach resulted in 17 experimental runs as shown in Table 2. The centre point for BBD model was selected based on the preliminary study which are 25% MEK concentration, 60 min operating time and 2-time coating cycle. For instance, 25% MEK concentration is within optimal range result high CO_2 flux. While the centre point for operation time and coating cycle did not result in the highest CO_2 flux but both parameters serve as a balanced point that allows for a comprehensive analysis of parameter space. The experiments were conducted systematically, and the flux was measured for each run. ANOVA has been conducted using built-in function in Design Expert 13.

Table 2: Experimental runs using BBD approach

Run	MEK concentration (mg/L)	Operating time (min)	Coating cycles	Flux ($mol/m^2.s$)
1	25	30	1	1.70
2	25	30	3	1.40
3	40	60	1	1.38
4	25	60	2	1.38
5	25	90	3	1.28
6	25	60	2	1.38
7	25	60	2	1.38
8	25	90	1	1.42
9	10	30	2	1.42
10	40	90	2	1.00
11	10	60	1	1.40
12	40	60	3	1.30
13	10	60	3	1.38
14	25	60	2	1.38
15	40	30	2	1.38
16	10	90	2	1.36
17	25	60	2	1.38

In this study, the RSM was employed using a BBD design to optimise coating parameters of the PVDF membrane for CO_2 flux. The experimental data were fitted to a second-order polynomial quadratic model. The quadratic equation representing the relationship between the CO_2 flux and the independent variable A, B and C is given by Equation (3).

$$\begin{aligned}\text{Flux} = 1.38 &- 0.0625A - 0.1050B - 0.0675C \\ &- 0.0800AB - 0.0150AC + 0.0400BC \\ &- 0.0875A^2 - 0.0025B^2 - 0.0725C^2\end{aligned} \tag{3}$$

Where A, B and C are the factors being studied such as MEK concentration, operating time and coating cycles, respectively. This model allows for the evaluation of both linear and interactional effects of the variables on the CO_2 flux, providing a comprehensive understanding of the optimisation process.

The ANOVA analysis results for the model fitting the optimisation of coating parameter for CO_2 flux using BBD reveal several key insights (see Table 3). The model has a significant F-value of 7.22 and *p*-value of 0.0081, indicating that the model is statistically significant. The R^2 value of 0.9028 suggests that approximately 90.28% of the variability in the CO_2 flux can be explained by the model, which demonstrates a good fit. The adjusted R^2 of 0.7778 accounts for the number of predictors in the model and suggests a slight lower but substantial explanatory power. However, the negative predicted R^2 of –0.5553 implies potential issues with the model ability to predict new observation accurately, which may be due to overfitting or an adequate model structure. According to Arimie et al., the significant gap between adjusted and predicted R^2 ($R^2 > 0.2$) caused by the presence of outliers leading to an inaccurate representation of the underlying relationship.[17] Among the individual terms, operating time (B) shows the highest significant with an F-value of 23.84 and *p*-value of 0.0019, indicating a strong effect on CO_2 flux. MEK concentration (A) and coating cycle (C) also significantly impact the response, with *p*-values of 0.0228 and 0.0164, respectively. The quadratic terms A^2 and B^2 are significant, indicating that the relationship between these factors and the response is not purely linear. The interaction terms AB, AC and BC with *p*-value above 0.05, are not significant, suggesting that the interaction between these parameters do not significantly affect CO_2 flux within the studied range. The model adequacy is supported by the adequate precision ratio of 13.2897, which is well above the threshold of 4, indicating a desirable signal-to-noise ratio and the model's capability to navigate the design space effectively. The relatively low standard deviation 0.0608 and coefficient of variation 4.43% further confirm the model reliability and precision in predicting the response variable. Overall, the analysis suggests that while the model is significant and fits the data well, further refinement may be needed to improve its predictive power, particularly addressing the negative predicted R^2. This could involve exploring additional factors, expanding the experimental range or employing different modelling approaches.

Table 3: Summary of ANOVA

Source	Sum of squares	df	Mean square	F-value	*p*-value	
Model	0.2405	9	0.0267	7.2200	0.0081	significant
A-MEK concentration	0.0313	1	0.0313	8.4500	0.0228	
B-Operating time	0.0882	1	0.0882	23.8400	0.0018	
C-Coating cycles	0.0365	1	0.0365	9.8500	0.0164	
AB	0.0256	1	0.0256	6.9200	0.0339	
AC	0.0009	1	0.0009	0.2432	0.6370	
BC	0.0064	1	0.0064	1.7300	0.2299	
A^2	0.0322	1	0.0322	8.7100	0.0214	
B^2	0.0000	1	0.0000	0.0071	0.9352	
C^2	0.0221	1	0.0221	5.9800	0.0444	

(*Continued on next page*)

Table 3 (*Continued*)

Source	Sum of squares	df	Mean square	F-value	*p*-value
Residual	0.0259	7	0.0037		
Lack of fit	0.0259	3	0.0086		
Pure error	0.0000	4	0.0000		
Cor total	0.2664	16			
Fit statistics					
Std. dev. : 0.0608	R^2 : 0.9028				
Mean : 1.37	Adjusted R^2 : 0.7778				
C.V. % : 4.43	Predicted R^2 : −0.5553				
	Adeq. precision : 13.2897				

3.5 Interaction between Coating Parameters

The 3D contour plots illustrate the interaction between different studied parameters affecting the CO_2 flux of PVDF membrane. Figure 5(a) shows the interaction between MEK concentration and operating time. The flux increases initially with both parameters, reaching an optimal range before declining. This indicates a synergistic effect where moderate MEK concentration and operating time jointly enhance the membrane flux towards CO_2. The increase in MEK concentration improves the dissolution and even distribution of PP solution. However, the contours indicate a peak followed by a decline, signifying that beyond a certain level, either an increase in MEK concentration or operating time led to over-coating, which reduces CO_2 flux. This behaviour is a saddle point, where an optimal region exists for maximum flux, beyond which performance deteriorates.[18]

Figure 5(b) shows the interaction between coating cycle and MEK concentration. The CO_2 flux rises when increase in the coating cycles and MEK concentration and then decreases. This suggests that a balanced number of coating cycles with an optimal MEK concentration yields the best result. Too many coating cycles lead to thick and denser coatings. The contour lines form ellipses, indicating that maintaining MEK concentration within an optimal range while controlling the number of coating cycles can prevent over-coating and ensure permeable membrane structure.[19]

Figure 5(c) depicts the interaction between operating time and coating cycles. CO_2 flux increases initially with moderate operating time and coating cycles, reaching an optimal point before declining. This behaviour underscores the importance of finding a balanced combination of these parameters.

The contour lines show that shorter operating times and fewer coating cycles are preferable to avoid excessive coating thickness. Prolonged operating times with multiple coating cycles can lead to dense and impermeable coatings, reducing membrane efficiency.[20]

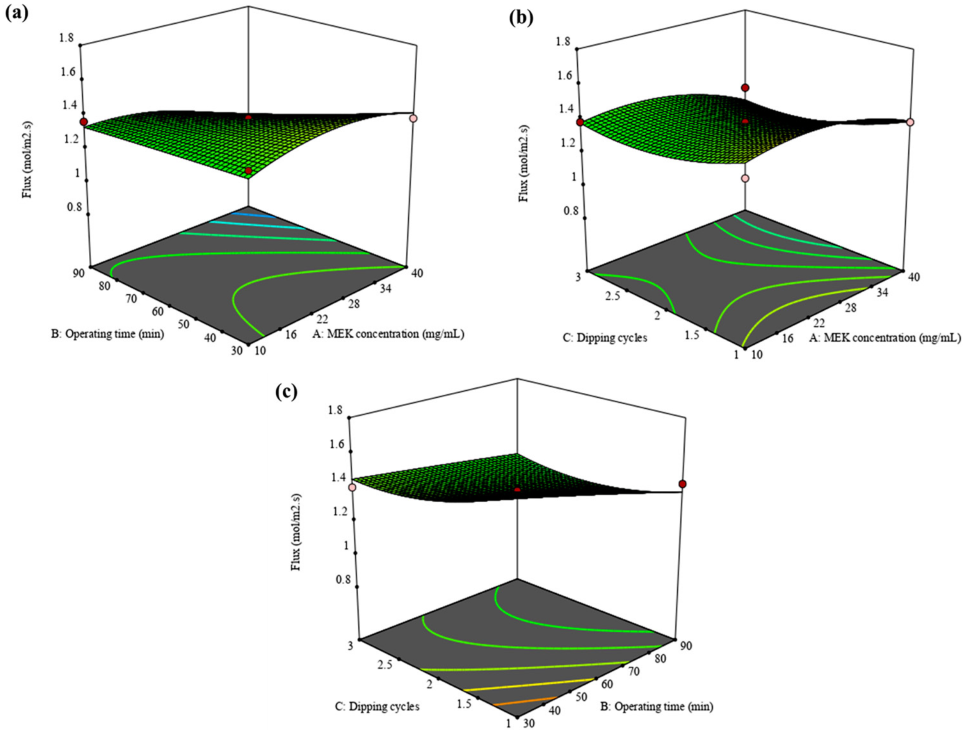

Figure 5: Interaction parameters between (a) MEK concentration and operating time, (b) coating cycle and MEK concentration and (c) operating time and coating cycles.

3.6 Optimisation and Desirability Analysis

In this study, the optimisation of coating parameters for PVDF membrane was carried out using Design Expert software. The goal was to maximise the CO_2 flux using RSM with a BBD. The desirability function approach was employed to identify the optimal combination of factors that satisfy the multiple response criteria. The individual response goals were defined, and their respective importance weights were assigned. The optimisation analysis yielded several solutions, each with a corresponding desirability score, indicating the overall suitability of the solution in meeting the desired objectives. Among the various solutions, the combination of 25% MEK concentration, an operating time of

30 min and 1 coating cycle was found to result in the highest desirability score of 0.945. This indicates that this specific set of conditions provides the best balance between the responses.

4. CONCLUSION

This study focused on optimising the coating parameter for PVDF hollow fiber membrane for CO_2 flux using BBD, examining MEK concentration, operation time and coating cycles. Results demonstrated that each parameter significantly impacts the CO_2 flux. MEK concentration ensures homogenous distribution of PP coating solution, appropriate operating time allows sufficient interaction without over-coating and a balanced number of coating cycles enhance the structure without resulting in dense coating. Contour plot revealed quadratic relationships, highlighting the need to fine-tune each parameter to achieve maximum CO_2 flux. The use of BBD enables efficient exploration of the coating parameters. Further work should be undertaken for further investigation of the applicability to different separation processes and membrane configurations, ensuring continued advancements in CO_2 capture technology.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support and facilities provided by the Ministry of Higher Education Malaysia (MoHE) through the Fundamental Research Grant Scheme (FRGS/1/2020/TK0/USM/01/4, 203.PJKIMIA.6071484) for providing research materials and financial through Graduate Research Assistance for Mohd Hazarel Zairy Mohd Harun and Universiti Sains Malaysia.

6. REFERENCES

1. Zainuddin, M. I. F. & Ahmad, A. L. (2022). Impact of dope extrusion rate and multilayer polydimethylsiloxane coating on asymmetric polyethersulfone hollow fiber membrane for CO_2/N_2 and CO_2/CH_4 separation. *Asia-Pac. J. Chem. Eng.*, 17(6), e2829. https://doi.org:https://doi.org/10.1002/apj.2829
2. Buddin, M. M. H. S. & Ahmad, A. L. (2022). Influence of formulation and spinning conditions on the morphology of PES and PES/ZIF-8 hollow fiber membrane. *Appl. Nanosci.*, 12, 3287–3296. https://doi.org:10.1007/s13204-022-02682-5
3. Wu, X. et al. (2021). Preparation and characterization of superhydrophobic PVDF/HMSNs hybrid membrane for CO_2 absorption. *Polym.*, 214, 123242. https://doi.org/10.1016/j.polymer.2020.123242

4. Toh, M. J. et al. (2020). Preparation of polydimethylsiloxane-SiO_2/PVDF-HFP mixed matrix membrane of enhanced wetting resistance for membrane gas absorption. *Sep. Purif. Technol.*, 244, 116543. https://doi.org/10.1016/j.seppur.2020.116543
5. Hassan, A. I. et al. (2021). Fabrication of polydimethylsiloxane (PDMS) dense layer on porous polyethersulfone (PES) hollow fibre membrane with varying dip coating parameters. *J. Phys. Sci.*, 32(1), 39–56. https://doi.org/10.21315/jps2021.32.1.4
6. Sun, X. et al. (2024). Improved ionic conductivity and cycling stability via composite separator constructed by coating organic-modified sepiolite/PVDF layer on PP via electrospinning technology. *Colloids Surf. A Physicochem. Eng. Asp.*, 691, 133925. https://doi.org/10.1016/j.colsurfa.2024.133925
7. Ahmad, A. L., Hassan, A. I. & Peng, L. C. (2022). Non-solvent influence of hydrophobic polymeric layer deposition on PVDF hollow fiber membrane for CO_2 gas absorption. *Membranes*, 12(1), 41. https://doi.org/10.3390/membranes12010041
8. Chin, J. Y. et al. (2021). Slippery membrane surface tuning with polypropylene coating to treat real aquaculture wastewater in membrane distillation. *Sci. Total Environ.*, 794, 148657. https://doi.org/10.1016/j.scitotenv.2021.148657
9. Harun, M. H. Z. M. & Ahmad, A. L. (2023). Optimization of ibuprofen and sulfamethoxazole extraction in green diluent liquid membrane using Plackett-Burman and Box Behnken designs. *J. Mol. Liq.*, 390, 123084. https://doi.org/10.1016/j.molliq.2023.123084
10. Mohamad Esham, M. I. et al. (2024). Remediation of oily-produced water from high-salinity oilfield using a low-cost, high-alumina calcium bentonite hollow fiber membrane. *J. Environ. Manage.*, 358, 120894. https://doi.org/10.1016/j.jenvman.2024.120894
11. Harun, M. H. Z. M. & Ahmad, A. L. (2022). Optimisation of ibuprofen extraction by emulsion liquid membrane using Box-Behnken Design. *J. Phys. Sci.*, 33(2), 95–105. https://doi.org/10.21315/jps2022.33.2.6
12. Raza, A. et al. (2021). Thickness effect on permeance of CO_2/CH_4 gases in CA coated PVDF composite membranes. *Trans. Indian Ceram. Soc.*, 80(2), 89–95. https://doi.org/10.1080/0371750X.2021.1880969
13. Tekell, M. C. et al. (2024). Controlling hydrophobicity of colloidal silica to promote miscibility in polymer nanocomposites. *Macromolecules*, 57(10), 4963–4977. https://doi.org/10.1021/acs.macromol.4c00279
14. Zelner, M. et al. (2021). Mixed-charge polyelectrolyte complex nanofiltration membrane: Preparation, performance and stability. *J. Membrane Sci.*, 636, 119579. https://doi.org/10.1016/j.memsci.2021.119579
15. Mavukkandy, M. O. et al. (2020). Thin film deposition techniques for polymeric membranes–A review. *J. Membrane Sci.*, 610, 118258. https://doi.org/10.1016/j.memsci.2020.118258
16. Bi, L. et al. (2024). MXene functionalized kevlar yarn via automated, continuous dip coating. *Adv. Funct. Mater.*, 34(14), 2312434. https://doi.org/10.1002/adfm.202312434

17. Arimie, C. O., Biu, E. O. & Ijomah, M. A. (2020). Outlier detection and effects on modeling. *OALib. J.*, 7(9), 30. https://doi.org/10.4236/oalib.1106619

18. Machado, J. C. B., Ferreira, M. R. A. & Soares, L. A. L. (2021). Optimization of the drying process of standardized extracts from leaves of *Spondias mombin* L. using Box–Behnken Design and response surface methodology. *J. Food Process. Preserv.*, 45, e15595. https://doi.org/10.1111/jfpp.15595

19. Khalil, A. & Kashif, M. (2021). Use of Box-Behnken Design for the nuclear magnetic resonance study of molecular complex of anticonvulsant drug with N,N-dimethylformamide and its application in quantitative analysis. *J. Molecular Liq.*, 326, 115308. https://doi.org/10.1016/j.molliq.2021.115308

20. Gao, N. et al. (2021). Double-layer peelable coating with eminent mechanical properties and anti-permeability. *Prog. Org. Coat.*, 160, 106517. https://doi.org/10.1016/j.porgcoat.2021.106517