

PAPER • OPEN ACCESS

Performance profiling of UV-grafted forward osmosis polyethersulfone membrane using multivariate classical scaling technique

To cite this article: A F H A Rahman *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **702** 012043

View the [article online](#) for updates and enhancements.

You may also like

- [Characterization of Polydopamine-Coated Polyethersulfone \(PES\) membrane for water purification](#)
Syawaliah, S Mulyati, Muzaitun et al.
- [Fabrication of Polyethersulfone \(PES\) Membrane Incorporated with Graphitic Carbon Nitride \(g-C₃N₂\) Nanoparticles in Palm Oil Mill Effluent \(POME\) Wastewater Treatment](#)
Cheong Kin Wai, Leong Kah Hon and Ling Wong Yong
- [Polyethersulfone/MWCNT nanocomposite scaffold for endometrial cell culture: preparation, characterization, and in vitro investigation](#)
Ali Alirezaei Alavije, Farid Barati, Mohammad Barati et al.



The advertisement features a dark teal background. On the left, the ECS logo is displayed above the text 'The Electrochemical Society' and its tagline 'Advancing solid state & electrochemical science & technology'. Below this, the event details are listed: '242nd ECS Meeting', 'Oct 9 – 13, 2022 • Atlanta, GA, US', and 'Presenting more than 2,400 technical abstracts in 50 symposia'. In the center, there is a portrait of M. Stanley Whittingham, a Nobel Laureate, with a small image of the Nobel Prize medal below it. To the right of the portrait, the text reads 'ECS Plenary Lecture featuring M. Stanley Whittingham, Binghamton University Nobel Laureate – 2019 Nobel Prize in Chemistry'. In the top right corner, there is a circular icon with a checkmark and the text 'Register now!'. The background of the advertisement is composed of two images: the top right shows a large audience seated in a lecture hall, and the bottom right shows a person in a white lab coat holding a glowing hexagonal interface with various scientific icons.

Performance profiling of UV-grafted forward osmosis polyethersulfone membrane using multivariate classical scaling technique

A F H A Rahman¹, M Y Mohd Yunus^{1,2}, T S L M T A Nasaruddin^{1,2}, N Harun¹
and M N Abu Seman^{1*}

¹Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.

²Earth Resource & Sustainability Center, Universiti Malaysia Pahang, Malaysia.

*E-mail: mazrul@ump.edu.my

Abstract. In this work, Classical Scaling (CMDS) method was used to develop a set of membrane profile performance for various types of UV-grafted polyethersulfone (PES) membrane. Previously, there is no such profiling has been considered. The main motivation of the profiling is to determine what is the most preference impact factor which significantly influence the membrane strength during application. Initially, nine (9) different samples of modified PES membranes were prepared mainly by adopting numerous characterization parameters of acrylic acid monomer concentration and grafting time. Three (3) performance indicators namely water permeability (A), solute permeability (B) and structural parameter (S) were used as representing the foundation of membrane performance profile. In particular, the Euclidean and City-block scales were utilized to build up the multivariate profile based on two dimension configurations. The key finding suggests that the modified membranes were easily clustered based on its grafting mechanism. From the general observation on the compressed CMDS dimensional space, samples that fall above the x-axis in Euclidean scale configuration and those scattered samples in the City-block scale have relatively larger pores. Thus, the CMDS profiling tends to favor the pore size as the dominant impact factor in characterizing the membrane performance based on the three specified parameters that investigated.

1. Introduction

A membrane is a semi-permeable barrier that shows different selectivity between species. Membrane separation process is a process utilized as a part of separation between different phases coexists in one system. The main target in this process is to selectively allow a species to permeate through the membrane freely while preventing the permeation of other components. However, some limitations such as membrane fouling, scaling, and concentration polarization have make the process of choosing and cleaning of membrane to take longer time and somewhat need to spend some cost for regular maintenance.

An approach to make an initial guess on the membrane to be chosen for future works is proposed which is by creating a membrane profile. Based on the literature survey made, the membrane profiling is only limited to the plasma membrane which have been studied by Peirce et al. [1], Weekes et al. [2],



and Hsu et al. [3]. However, no attempt to generate a membrane profiling for forward osmosis membrane has been done. In the current work, the multidimensional scaling (MDS) method is used to create membrane profiling on pore size effect prediction of the polyethersulfone (PES) membrane.

Profiling has become a way of seeing an outline of something in a clear, simple, and more precise way. It is in general defined as a depiction of something that gives us a picture of the overall system of it. A profile can be treated as an initial guess of generic trending on the respective subject that investigated. In the field of membrane technology, however, limited studies of profiling performance are observed.

In this study, a membrane profile that derived from the intrinsic properties of the NF-PES membrane is proposed. This profile is mainly developed by means of multivariate scores as it involves the investigation of various samples based on multiple sets of contributory factors. In this respect, Classical Scaling (CMDS) is one of the multivariate techniques that typically utilized to extract the essence of pattern based on a specific data set [4]. It is usually employed for envisioning the level of similarity or dissimilarity among individual cases, which display the latent information in the form of distance configuration matrix. Thus, the main goal of this study is to create a membrane profiling for pore size effect prediction of the FO membrane based on their intrinsic properties namely water permeability coefficient (A), solute permeability coefficient (B), and structural parameter (S).

2. Profiling Frameworks based on Classical Scaling Approach

The general procedures of developing the multivariate scores of Classical Scaling (CMDS) in this work was adopted from Mohd Yunus [5]. Firstly, the squared dissimilarity matrix, Δ_2 is determined based on $\mathbf{X}_{n \times m}$, (where n : samples, m : variables) using a particular distance measure (scale) through the application of major product moment of matrix operation. In principle, the size of matrix Δ_2 is directly determined by the magnitude of samples, 'n' as shown in the equation (1).

$$\Delta_{n \times n} = \Delta_2 = \begin{bmatrix} \delta_{1,1} & \delta_{1,2} & \dots & \delta_{1,n} \\ \delta_{2,1} & \delta_{2,2} & \dots & \delta_{2,n} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \delta_{n,1} & \delta_{n,2} & \dots & \delta_{n,n} \end{bmatrix} \quad (1)$$

In this study, the basis scale of developing the multivariate score configurations CMDS are Euclidean and City-block distances as shown in equations (2) and (3).

$$\text{Euclidean distance: } \delta_{ij} = \left\{ \sum_a (x_{ia} - x_{ja})^2 \right\}^{\frac{1}{2}} \quad (2)$$

$$\text{City-block distance: } \delta_{ij} = \sum_a |x_{ia} - x_{ja}| \quad (3)$$

where δ_{ij} is the dissimilarity measure between objects i and j , x represents the original Cartesian coordinate of those objects (samples), and a is the number of axes in the original space. The motive of applying two types of different scales is for profiling verification. Next the double-centered matrix, \mathbf{B}_Δ , is computed on Δ_2 as in equation (4).

$$\mathbf{B}_\Delta = -\frac{1}{2} \mathbf{J}_n \Delta_2 \mathbf{J}_n \quad \text{where } \mathbf{J}_n = (\mathbf{I}_n - \mathbf{1}_n \mathbf{1}_n' / n) \quad (4)$$

where \mathbf{I}_n is an identity matrix of size $n \times n$, while $\mathbf{1}_n$ is a vector of size 'n' with all elements equal to 1. Additional remarks on \mathbf{J}_n are provided in Mohd Yunus [5].

\mathbf{B}_A is then decomposed into Eigen basic structure through the employment of singular value decomposition (SVD) technique particularly in producing eigenvectors and eigenvalues of Λ_2 that depicted by equation (5). Lastly, the multivariate scores based on Cartesian coordinates, \mathbf{X}_E , is developed based on equation (6).

$$\mathbf{B} = \mathbf{U}\mathbf{V}\mathbf{U}^T \quad (5)$$

where U and V are the Eigen vectors and Eigen values respectively.

$$\mathbf{X}_E = \mathbf{U}_+ \mathbf{V}_+^{0.5} \quad (6)$$

where $\mathbf{V}_+^{0.5}$ is a diagonal matrix with all positive elements of $v^{0.5}$ and \mathbf{U}_+ is the corresponding sets of eigenvectors.

3. Case Study: FO Using NF-PES Membrane

In the experiment, the nanofiltration polyether sulfone (NFPES) membrane was purchased from Amfor Inc (China). The membrane was modified using two parameters, namely acrylic acid (AA) monomer concentration and UV grafting time. For the profiling purpose, the data used were water permeability (A), solute permeability (B) and structural parameter for membrane (S). The membrane S-value is a measure of the resistance of the membrane's support layer towards solute diffusion. These all data of A, B, and S were taken from Rahman [6]. Sets of data obtained are shown in table 1. These data are then inserted into the workspace section in MATLAB. Euclidean distance was employed to measure the dissimilarity between all samples.

Table 1. Data used in membrane profiling [6].

Membrane type	Sample number	A (L/ m ² .h.bar)	B (m/h)	S (mm)
Unmodified NF-PES	1	9	0.01540	28.02
5AA-1	2	7.37	0.02930	8.11
15AA-1	3	10.67	0.02326	12.54
30AA-1	4	6.91	0.01915	8.2
50AA-1	5	7.91	0.07898	8.1
5AA-5	6	6.84	0.02808	7.87
15AA-5	7	8.39	0.02462	8.26
30AA-5	8	7.39	0.11725	5.89
50AA-5	9	7.89	0.02516	12.51

*5AA-1 represents (concentration in g/L)AA-(time for UV grafting in minute)

4. Results and Discussion

In this work, all data were first converted to a dissimilarity matrix according to the procedure mention in section 3. Figure 1 shows the dissimilarity matrix generated by MATLAB. The points are then being mapped down in two-dimensional space such that the 'straight line' (Euclidean) distances as shown in figure 2. It is observed that S8 has the largest distance from S1 (4.6173) in relative to the other samples. The reproduction of scores for figure 1 is illustrated in figure 3 in which location of S8 is seen diverts far away from S1 in contrast to other samples. The dissimilarities are basically due to the modifications made on the membranes.

Mat_E =								
0	3.2786	2.6960	3.4207	3.6026	3.5101	2.9916	4.6173	2.4984
3.2786	0	2.8252	0.4825	1.5084	0.4432	0.8586	2.5708	0.7928
2.6960	2.8252	0	3.1921	2.8815	3.2600	1.9987	3.9783	2.3105
3.4207	0.4825	3.1921	0	1.9232	0.2698	1.2399	2.8920	1.0505
3.6026	1.5084	2.8815	1.9232	0	1.7230	1.6257	1.2350	1.6923
3.5101	0.4432	3.2600	0.2698	1.7230	0	1.2930	2.6414	1.1152
2.9916	0.8586	1.9987	1.2399	1.6257	1.2930	0	2.8327	0.7561
4.6173	2.5708	3.9783	2.8920	1.2350	2.6414	2.8327	0	2.8752
2.4984	0.7928	2.3105	1.0505	1.6923	1.1152	0.7561	2.8752	0

Figure 1. Dissimilarity matrix gained from MATLAB for Euclidean Distance.

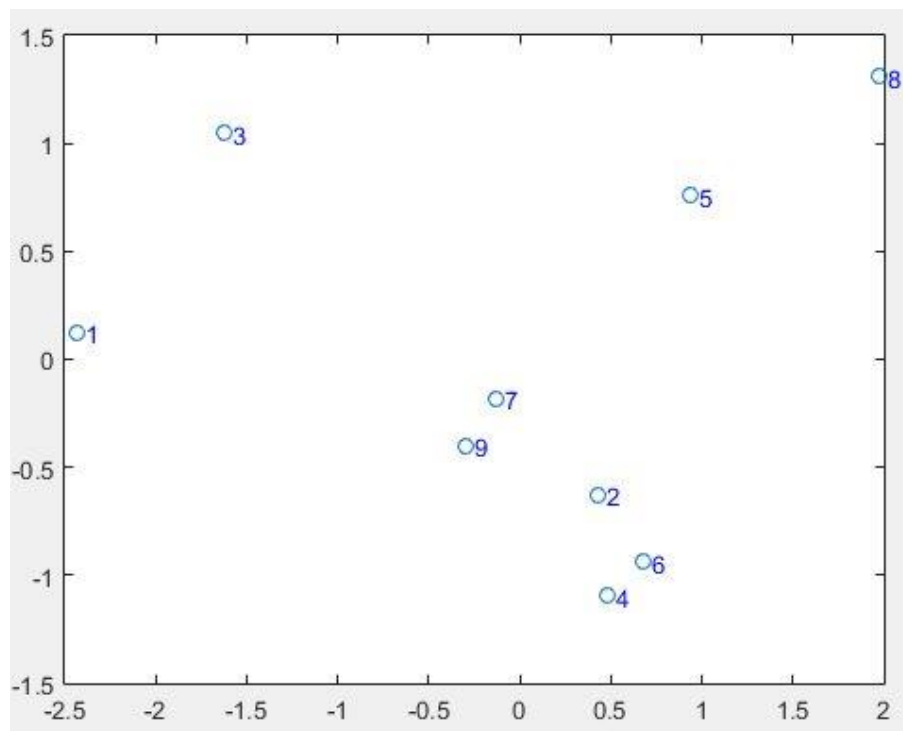


Figure 2. Membrane Profile using Euclidean Distance.

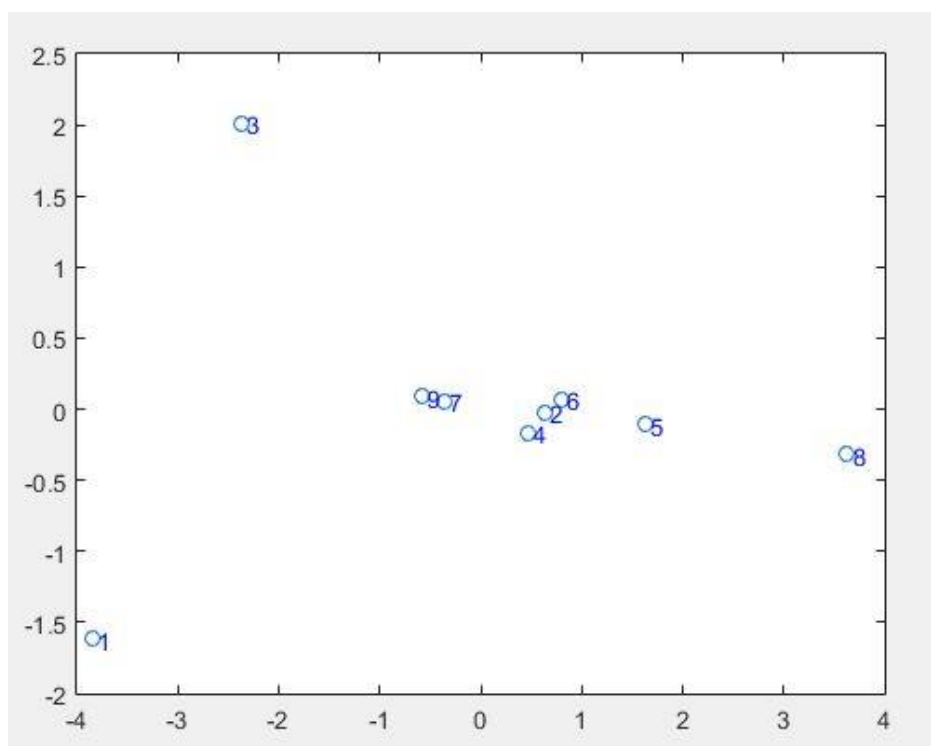


Figure 3. MDS Scores for Forward Osmosis Membranes Profile using City Block Distance.

The x-axis in figures 2 and 3 represents dimension 1, and y-axis represents dimension 2. From figure 2, it is observed that there are two division exist. The first one is those that falls below the x-axis which composed of samples 2, 4, 6, 7, and 9, and the second one is those that falls above the x-axis which composed of samples 1, 3, 5, and 8. As from figure 3 (City-block distance), there is a group cluster exists and four singletons namely sample 1, 3, 5, and 8. Comparing both figures, it is observed that the circled samples in figure 3 represents the samples that are located below the x-axis in Euclidean distance. Through result analysis for both distance measured, the overall trend suggests that the performance of City-block can be considered comparable to the Euclidean scale.

As for justifying the results shown in figures 2 and 3, for the sample 1 (unmodified membrane), Abu Seman et al. [7] found that the unmodified membrane exhibited higher flux compared to the modified membrane as the unmodified membrane has a relatively larger pores than modified membrane. The other samples in the same group are sample 5 (50AA-1min) and sample 8 (30AA-5min). According to Rahman [6], a detrimental effect was recorded for both sample in which it both membrane performances got affected. This membrane performance reduction is due to the increase of pore size as the PES membrane is dependent on the pH value [8]. Pore enlargement occurs as the pH decrease. Sample 6 (5AA-5min) has the lowest monomer concentration tested with highest UV-grafting time.

According to Rahman [6], during the immersion process when the monomer concentration is low, some molecules would penetrate the membrane and then undergo polymerization process. These molecules will lead to the reduction of membrane pores as it grafted in both membrane surface and deep within the pores. More compact membrane matrix could be developed which maximized the amount of effective grafting and its penetration inside the pores [7]. As the effective grafting time increased, the pore size will be reduced, and lead to the reduction of water permeability. Sample 4 (30AA-1min) somehow turned out the same even though the monomer concentration is huge different. Although grafted at high concentration of monomer, the effective grafting exceeds the chain scission. This is due to the low grafting time. It can be concluded that, as the effective grafting exceeds, the pore could probably reduce due to the more compact membrane was developed. This can be correlate with sample

6. For sample 3 (15AA-1min), according to Rahman [6], the water flux for the sample increased after UV-grafting which is caused by the pore enlargement mechanism. The membrane faced a severe pore enlargement due to the extensive chain scission [9].

As what has been observed and studied, the pore size effect has seemed to suit the profile so well. The pore size could either have enlarged or reduced depending on which quarter inside the profile the sample falls into, and by interpreting those data in terms of multidimensional scaling, a clearer info regarding the data could be revealed in a much simpler way. Recall back figures 2 and 3. The samples that falls above the x-axis (1, 3, 5, 8) in figure 2 shows that they all experience pore enlargement by some factors during the process. In comparing to figure 3, those scattered sample (1, 3, 5, 8) are also the group that occur pore enlargement.

5. Conclusions & Recommendations

A profiling on a set of data has been applied using MDS method. Three parameters have been considered in creating the profile namely water permeability, solute permeability, and structural parameter. Euclidean distance was used as the base of calculation. From the result, it can be concluded that, those samples that fall above the x-axis in Euclidean scale and those scattered samples in City-block scale have relatively larger pores than those below the x-axis. This happened due to some the effect of grafting time and monomer concentration. It is shows that certain limitations are seen to make an important factor to be considered when making a membrane profile.

Those factors include the sensitivity analysis and the distinctive properties of the membrane. For future works, it is suggested that those factors are being considered for a better accuracy of the result. Another method that is widely used as a multivariate tool is the Principal Component Analysis (PCA). With insignificant extra exertion PCA gives a guide to how to decrease a complex informational index to a lower dimension to uncover the occasionally covered up, improved progression that regularly underlie it [10].

Acknowledgments

The authors wish to express numerous thanks to Universiti Malaysia Pahang and the Ministry of Higher Education through the financial aid from Postgraduate Research Grant Scheme PGRS:160336, Fundamental Research Grant Scheme FRGS/1/2016/TK02/UMP/02/8 (RDU160127).

References

- [1] Peirce M J, Wait R, Begum S, Saklatvala J and Cope A P 2004 Expression profiling of lymphocyte plasma membrane proteins *Mol. Cell. Proteomics* **3**(1) 56-65
- [2] Weekes M P, Antrobus R, Talbot S, Hör S, Simecek N, Smith D L and Lehner P J 2012 Proteomic plasma membrane profiling reveals an essential role for gp96 in the cell surface expression of LDLR family members, including the LDL receptor and LRP6. *J. Proteome Res.* **11**(3) 1475-84
- [3] Hsu J L, van den Boomen D J, Tomasec P, Weekes M P, Antrobus R, Stanton R J and Davison A J 2015 Plasma membrane profiling defines an expanded class of cell surface proteins selectively targeted for degradation by HCMV US2 in cooperation with UL141 *PLoS pathogens* **11**(4) e1004811
- [4] Cox T F 2005 *An Introduction to Multivariate Data Analysis* (Hodder Education. London Great Britain)
- [5] Mohd Yunus M Y 2012 *Multivariate statistical process monitoring using classical multidimensional scaling*. (Newcastle University)
- [6] Rahman A F H A and Abu Seman M N 2017 Surface Modification of Polyethersulfone (PES) membrane via UV-grafting for Forward Osmosis Technology *Malaysian J. Analytic. Sci.*
- [7] Abu Seman M N, Khayet M, and Hilal N 2012 Comparison of two different UV-grafted nanofiltration membranes prepared for reduction of humic acid fouling using acrylic acid and N-vinylpyrrolidone *Desalination* **287** 19-29
- [8] Deng B, Yang X X, Xie L D, Li J Y, Hou Z C, Yao S, Huang Q. 2009 Microfiltration membranes with pH dependent property prepared from poly(methacrylic acid) grafted polyethersulfone powder *J. Membrane Sci.* **330**(1-2) 363-68

- [9] Pieracci J, Crivello J V and Belfort G 2002 UV-assisted graft polymerization of N-vinyl-2-pyrrolidinone onto poly(ether sulfone) ultrafiltration membranes using selective UV wavelengths *Chem. Mat.* **14**(1) 256-65
- [10] Shlens J 2003 A tutorial on principal component analysis: derivation, discussion and singular value decomposition *Mar.* **25**(1) 16