DETERMINATION OF PORE CHARACTERISTICS AND MOLECULAR WEIGHT CUT-OFF (MWCO) OF UF MEMBRANES VIA SOLUTE TRANSPORT AND MATHEMATICAL METHOD

Dang Thi Thanh Huyen[1]*

Abstract: *The objective of this study was to explore a non-analytical but empirical and mathematical method for the determination of pore size and pore density of several polymeric tailor-made membranes. The proposed method used the fractional rejection concept of solute in membrane pores. Experiment was conducted with Polyethylene glycol PEG and PEO with different molecular weights as feed water, each feed solution had concentration of 100 mg/L, and applied ultrafiltration test with the LSMM PES based membranes. The data was interpreted using log-normal probability function model to describe the membrane sieving curves and the Hagen-Poiseuille equation for surface porosity/density. It was revealed that the solute transport method could provide relatively values of pore size and pore density for reference. It also proved the impacts of LSMM additives on membrane properties in which at low LSMM incorporation, the thinner membranes (0.2 mm thick) had higher mean pore size, accordingly higher the MWCO while at higher additive concentration, the opposite was observed.*

Keywords: *Pore characterization, solute transport method, surface additives, ultrafiltration membrane, MWCO.*

Received: September 6th, 2017; revised: October 20th, 2017; accepted: November 2nd, 2017

1. Introduction

Porous integrally-asymmetric membranes are often made by the phase inversion method [1,2]. This method is applied mainly in the preparation of membranes for dialysis, microfiltration (MF) and ultrafiltration (UF). Most commercial UF membranes are cast via this technique using a multi-component solution containing polymer(s), solvent(s) and non-solvent(s) or additive(s). In many cases, the pore characteristics (porosity, pore size) and skin layer morphology are modified by blending additives to the casting solution [3]. Characterization of membrane pores as well as the molecular weight cut-off (MWCO) of the membranes is very crucial as it impacts the retention capabilities of membranes to some extent. The MWCO, by definition, is the molecular weight that would yield 90% solute separation, or in other speaking, it is the lowest molecular weight (in Daltons) at which greater than 90% of a solute with a known molecular weight is retained by the membrane. For instance, membranes with MWCO of 30000 Dalton (or 30 kDal. in brief) can retain 90% of solutes having MW of 30kDal and higher MW.

In terms of pore characteristics, efficient membranes should have small pore sizes, high pore density and high surface porosity so that they can remove more contaminants such as humic substances from water, and yet achieve high permeation fluxes. Values of the average pore size, porosity and pore size distribution can be obtained by several techniques including solute transport, atomic force microscopy (AFM) and the bubble point method. The bubble point is a widely-recommended method for measuring pore sizes and testing the integrity of the membranes [4]. This method, nevertheless, had a limited use since its key assumption of a zero contact angle is not achieved. The air usually passed through the largest pore on membrane surface first, thus this technique was really a measure of the largest pore size [4]. The pore sizes also can be measured via AFM. They, however, were about 2-4 times higher than those by solute transport method [5,6]. The difference was explained by the characteristics of the two methods. The pore sizes obtained from a solute separation corresponded to a minimal size of the pore constriction experienced by the solute as passing through the pores, while pore sizes measured by AFM corresponded to the pore entrances which were of funnel shape and had maximum open at the entrance [7]. Of the three methods, the solute transport seems to be the most reliable technique and followed by AFM.

[1] Dr, Faculty of Environmental Engineering, National University of Civil Engineering.
** Corresponding author. E-mail: huyendtt@nuce.edu.vn.*

The key objective of this study is to study the pore characteristics and MWCO of several tailor-made membranes in the lab by solute separation method, since this method is cheaper and relatively precise compared to other methods using advanced equipment.

2. Methodology

2.1 Testing membranes

Five different membranes (0.5LSMM1, 0.5LSMM2, 4.5LSMM1, 4.5LSMM2 and Double LSMM) were PES based membranes integrated with hydrophilic additives LSMM (Low molecular weight surface modifying macromolecules), dissolved in N-methyl pyrrolidone NMP solvent and developed in the lab by a method which was described in details elsewhere [8,9]. For fabrication of membranes, the polymer solution (including 03 components: base polymer, additives and solvent) was cast by a casting knife on a clean glass plate, then the film was hardened in coagulation bath using ice water (4^{o}C). The thickness of film could be changed by adjusting the gap between casting knife and glass plate. Most of membranes (0.5LSMM1, 0.5LSMM2, 4.5LSMM1, 4.5LSMM2) were made via single cast step. Only the Double LSMM membranes had double casting steps to see the impact of casting method on pore characteristics of membranes. Morphological examination of the top surface and cross-section was made using scanning electron microscopy (SEM, model JSM-6400, Japan Electron Optics Limited, Japan). Properties of these membranes are presented in Table 1.

Table 1. *Properties of Tested membranes*

Type of membranes	PES (% by weight)	LSMM (% by weight)	NMP (%by weight)	Thickness of casting film (mm)	Casting method
0.5LSMM1	18	0.5	81.5	20	Single casting
0.5LSMM2	18	0.5	81.5	25	Single casting
4.5LSMM1	18	4.5	77.5	20	Single casting
4.5LSMM2	18	4.5	77.5	25	Single casting
Double LSMM	18	0.5	81.5	25	Double casting

All these membranes were cleaned thoroughly in ultra pure water and cut into 52-mm diameter coupons for testing in the ultrafiltration system.

2.2 Solute transport test

Solute transport test was essentially a continuation of the ultrafiltration test in which the feed was solutions of different known molecular weight solutes and the system was tested at different MW solute for one-hour periods at 50 psi. Diagram of solute transport test is presented in Fig. 1. The feed concentrations were 100 mg/L solutions of Polyethylene glycol PEG with molecular weights of 1.5, 6, 10, 14, 20, 35 kDal and polyethylene oxide PEO with molecular weight of 100 kDal. The PEG and PEO polymers were chosen for this solute transport test because they are synthetic polyethers that are readily available in a range of molecular weights. Moreover, they are amphiphilic and soluble in water. The feed was pumped through testing membranes (as described above) for one hour and the permeate was collected.

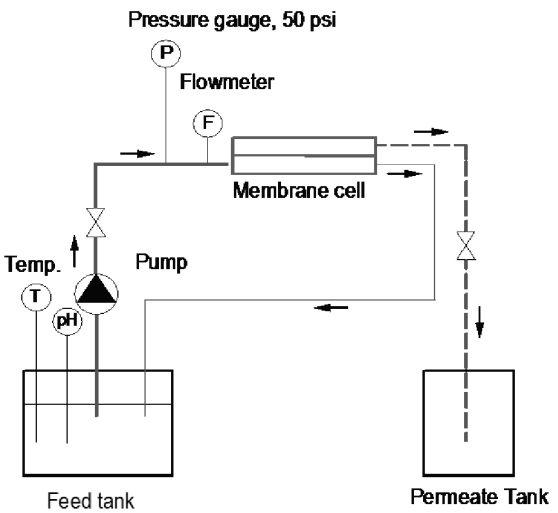


Figure 1. *Diagram of Solute transport test*

The membrane system was flushed with ultra-pure water for one hour after each PEG/PEO solution circulation tests. At the end of the hour, the permeate (the filtered water) was collected in the permeate tank and measured to corroborate that the solute transport tests had not altered the flux (i.e., fouled the membrane). Pressure was kept constant at 50 psi and monitored via pressure gauge.

The feed and permeate samples (during the run with PEG/PEO solutions) were collected and analyzed for DOC concentrations using a thermal oxidation-based DOC analyzer (Phoenix 9000, Teledyne-Tekmar, Mason, OH). The MWCO, which is the molecular weight that would yield 90% solute separation, was determined based on the solute transport data. These data were assessed using log-normal probability function model to describe the membrane sieving curves and the Hagen-Poiseuille equation for surface porosity [6]. This shall be described in details in the next section.

2.3 Derivation of solute transport data via Mathematical method

The calculation of porosity, pore density and mean pore size were referred from previous study [6]. Solute diameters were calculated from the following expressions for the Stokes radius (*a*) of PEG and PEO as a function of their molecular weights (*M*):

$$a_{PEG} = 16.73 \times 10^{-10} M^{0.557} \quad (1)$$

$$a_{PEO} = 10.44 \times 10^{-10} M^{0.587} \quad (2)$$

These equations were derived from empirical expressions of PEG and PEO's intrinsic viscosities and the Stokes-Einstein equation for diffusivity, assuming that the Stokes radius would diffuse at the same rate as the particle under study [6].

Based on the solute (PEG, PEO) separation data, the pore size distribution of the membranes was computed using the log-normal probability function. It is predicted to be an accurate way to describe UF membranes sieving curves, i.e., the solute separation, *f* (%), versus the solute diameter (d_s) follow the log-normal relationship:

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln\sigma_p \sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln(d_p/\mu_p)}{\ln\sigma_p}\right)^2\right] \quad (3)$$

where d_p is the pore diameter, μ_p is the geometric mean of the pore diameter and, σ_p is the geometric standard deviation (GSD) of the pore diameter. These parameters are denominated geometric, because they correspond to a log-normal distribution $\mu_p = d_s @ f = 50\%$ (solute diameter that correspond to 50% separation of PEG obtained from the PEG separation data), and σ_p, is calculated by:

$$\sigma_p = \frac{d_s @ f = 84.13\%}{d_s @ f = 50\%} \quad (4)$$

where d_s is the solute diameter ($d_p = d_s$). Their geometric means ($\mu_p = \mu_s$) and their geometric standard deviations (GSD) ($\sigma_p = \sigma_s$) were considered to be the same. μs is the geometric mean, and σ_s is the GSD of the solute diameter. Library functions from Microsoft Excel for the standard normal distribution and base-10 logarithm (i.e., NORMSINV and LOG10, respectively) were used to compute solute separation *f* (%) at a predetermined pore size base on PEG separation data. These *f* values were then used together with the value of μ_p and σ_p obtained from equation (4) to compute the pore size distribution of the membrane based on equation (3). This model is based on an assumption that dependence of solute separation on the steric and hydrodynamic interaction between solute and pores is ignored, thus the pore size equals the solute size [6].

Calculations of pore density (number of pores per unit area, N) and surface porosity (ratio of the area of pores to the total membrane surface area, S_p) were based on the Hagen-Poiseuille equation modified for a porous membrane, assuming laminar flow:

$$J_i = \frac{N_i \pi d_i^4 \Delta P}{128 \eta \delta} \quad (5)$$

where J_i is solvent flux for pores with diameter d_i (m^3/m^2-s); N_i is density of pores with diameter d_i (dimensionless); Δ*P* is pressure difference across the pores (Pa) (345 kPa in this study); η is solvent viscosity (N-s/m^2) ($\eta = 9.34 \times 10^{-4}$ at water temperature of 23°C); δ is length of the pores, considered equivalent to the thickness of the skin layer (no tortuosity) (m) (approximately $\delta = 2 \times 10^{-7}$ m).

Thus, total flux (J, i.e., the final PWP) through the membrane was the summation of all fluxes through the pores with different sizes:

$$J = \Sigma J_i = \frac{\pi \Delta P}{128 \eta \delta} \Sigma N_i d_i^4 = \frac{\pi \Delta P N}{128 \eta \delta} \sum_{d_{\min}}^{d_{\max}} f_i d_i^4 \quad (6)$$

where f_i is fraction of pores with diameter d_i.

Therefore, density of pores is calculated by:

$$N = \frac{128\eta\delta J}{\pi\Delta P\sum_{d_{\min}}^{d_{\max}} f_i d_i^4} \quad (7)$$

3. Results and Discussions

3.1 Pore characterization

Fig. 2 presents the sieving curves of the tested membranes. It is obvious that for low LSMM concentration (i.e., 0.5%wt LSMM), the thinner membranes (0.2 mm thick) had higher mean pore size, accordingly higher the MWCO. For a higher additive concentration (4.5 wt%), the opposite was observed. Membranes with 0.25mm thick were having higher mean pore sizes. The explanation of those phenomena may lie in the impact of shear stress. Since the shear stress is directly proportional to casting velocity, solution viscosity and inversely proportional to film thickness (Shear stress = (viscosity)*(velocity/thickness)), the shear stress increases by either increasing the casting velocity, increasing viscosity or by decreasing the thickness. High shear rate often leads to greater molecular orientation and leaves bigger gaps (pores) between two aligned macromolecular nodules. The pore sizes are therefore larger.

Table 2. *Pore characterization*

Membranes	MWCO (kDal)	Mean pore size (nm)	Pore density (# of pore/m^2)
Single cast LSMM*	91.40 ± 3.93	5.33 ± 0.63	5.26 ± 0.45
Double cast LSMM	81.21 ± 2.05	5.13 ± 0.07	6.33 ± 0.17

**Average of the four membranes made by single cast method (0.5LSMM1, 0.5LSMM2, 4.5LSMM1, 4.5LSMM2)*

According to Table 2, the double cast membranes caused a reduction in MWCO from 91 kDal to 81 kDal. Table 2 also shows that the mean pore sizes are slightly more than 5 nm for these membranes which are wider than those of the hydrophobic membranes as found in previous study [10]. It is worth noting that the log-normal probability model represents just an approximation of the actual pore size distributions, particularly for pore sizes of less than 2nm, where the conditions are not purely steric and hydrodynamic interaction between solute and pores may not be ignored [6]. Nevertheless, the pore size and pore size distribution presented above display correctly the changes caused by the different modes of dope casting. As the pore size is smaller, the pore density is therefore higher for the Double LSMM membranes.

Previous studies pointed out fascinatingly that the newly modified PES-LSMM membranes was in the range of tight UF membranes with relatively smooth surface, small pore size and MWCO of approximately 60 kDal [11]. In this study, the MWCO of PES LSMM membranes were more than 90 kDal with mean pore sizes varied as in Fig. 2. This once again confirms the fabrication conditions such as membrane thickness or casting methods could alter significantly the membrane properties.

The probability density function plot in Fig. 3 gives an indication of the pore size distribution for the different membranes. It seems that the addition of LSMM and membrane thickness did not provide clear impact on pore size. For instance, membranes with 0.5 %wt of LSMM (nominal thickness = 25mm) and membrane with 4.5%wt of LSMM (nominal thickness = 20mm) had similar mean pore size of 3 nm, which was less than mean pore size of 4.8 nm of the remaining membranes. It is observed that those membranes, that had larger

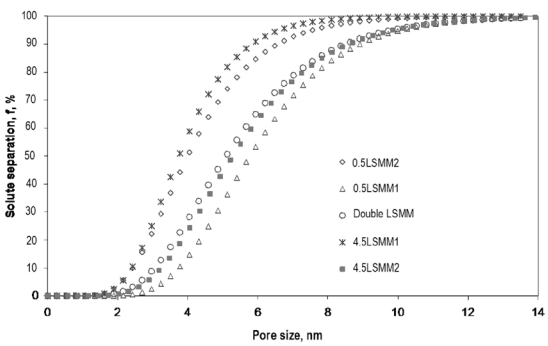


Figure 2. *Sieving curves of LSMM membranes*

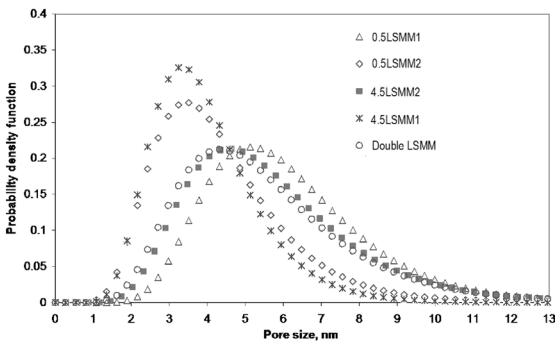


Figure 3. *Pore size distribution of LSMM membranes*

mean pore sizes, had a smaller most probable size of the pores (maximum in the probability density function curves). It is worth noting that the pore size distributions in Fig. 3 represents just an approximation of the actual data because they simulates from the mathematical equations with some assumptions that membranes are purely steric and hydrodynamic interaction between solute and pores is ignored.

According to Table 2 and the Figs. 1 and 2, some conclusions and interpretations about the impact of manufacturing conditions on pore characteristics can be made as following: (i) Thicker membranes lead to lower shear stress, accordingly smaller pore sizes and MWCO and (ii) Double casting method increases the porosity of membrane with the same amount of SMM additive again due to the effect of shear stress as explained above.

3.2 Correlation of pore characteristics and casting methods

The impact of the new casting method on the morphology of the double casting ultrafiltration membranes was investigated. SEM micrographs presenting the surfaces and cross-sections of the samples are depicted in Fig. 4. All the images were captured at a magnification of 1000.

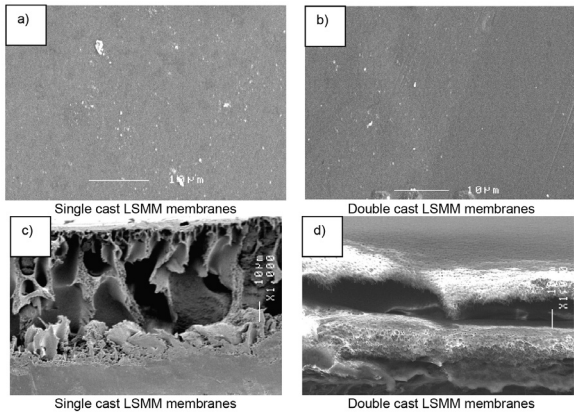


Figure 4. *SEM images of membranes: top surface (a, b); cross-section (c, d)*

There seems to be no appreciable surface variations between membranes made by single or double casting methods (Figs. 4a and 4b). Only in the cross-section micrographs, did a two-layer spongy structure appear for the new casting method (Figs. 4c and 4d). This is something expected as the second casting motion was done on top of the surface generated by the first casting motion. The gap between two layers (Fig. 4c) may lead to some positive changes in membrane characteristics and performance, since the single cast membrane very clearly exhibits large finger like cavities. These macro voids should be avoided whenever possible since they may rupture quickly or they are more susceptible to compaction under a high pressure. Although the macro voids do not exist in the Double LSMM membranes, a larger portion of the cross-section seems to have more solid structure. The effect of the presence of the gap between two solid layers on the membrane performance is still unknown.

As observed in the SEM image, the Double cast LSMM membrane has two layers of spongy structure, which may lead the smaller mean pore sizes and MWCOs. However, based on Table 2, there is no significant difference in the pore size of these membranes. It then can be said that SEM is not a good indicator in examining the pore sizes of membranes.

3.3 Correlation of pore size and MWCO

Effort was made to consider if there was any correlation between MWCO and pore characteristics. From Fig. 5, there was a clear trend that as MWCO increased, the mean pore size increased. It completely follows the logical concept of membrane technology since MWCO is defined as the molecular weight that yields 90% solute separation and smaller MWCO values are only obtained for membranes having smaller pore sizes. Cho et al. [12] also reported that an effective MWCO is not usually the same as a nominal MWCO provided by the manufacturer. It may be explained by the fact that to yield similar fluxes, membranes with smaller pores (smaller MWCO) often have higher pore densities. The tailor-made membranes, which had MWCO of approximately 90 kDal, had a low MWCO, small mean pore size and high pore density. It was proved in previous study [13] that the effective MWCO of the membranes was much lower than the MWCOs measured in this work while the MWCO measured by solute transport were often lower than the data provided by the

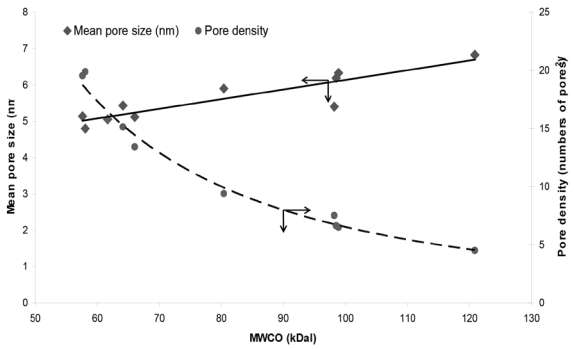


Figure 5. *Correlation of MWCO and pore characteristics*

manufacturers [12,14]. The effects of electrostatic repulsion and hydrodynamic operating conditions are potential reasons for this discrepancy [14].

4. Conclusion

Size exclusion plays a major role in the solute rejection of a membrane based on its pore size and the solute molecular size. The pore size and its distribution have been measured using various methods including the bubble point method, liquid displacement, solute probe techniques, and many others. In this study, the pore characteristics of Ultrafiltration membranes were promisingly determined via solute transport test and mathematical calculations without using any equipment or analytical machine. This method however just gives the approximation in terms of pore size and pore density as it has some assumptions on ignoring of influence of the steric and hydrodynamic interaction between PEG and pore sizes on solute rejection. In fact, there are always some interactions between solutes and membranes to some certain extents.

The additives of LSMM had a visible effect on MWCO and porosity. However, the pore size of LSMM membranes varied with the different percentage of LSMM in the casting solution and the casting method (single versus double casting). Thicker membranes lead to lower shear stress, accordingly smaller pore sizes and MWCO. Double casting method increases the porosity of membrane with the same amount of LSMM additive.

Reference

1. Kesting R.E. (1971), *Synthetic Polymeric Membranes*, McGraw-Hill Book Company, New York, NY.

2. Matsuura T. (1994), *Synthetic Membranes and Membrane Separation Processes*, CRC Press, Boca Raton, FL.

3. Pinnau I., Freeman B.D. (2000), *Membrane formation and modification overview*, American Chemical Society, Washington, DC.

4. Cheryan M. (1986), *Ultrafiltration Handbook*, Technomic Publishing Com., Lancaster, PA.

5. Khayet M., Suk DE., Narbaitz RM, Santerre JP, Matsuura T. (2002), "Study on surface modification by surface-modifying macromolecules and its application in membrane separation processes", *Journal of Applied Polymer Science*, 89:2902-2916.

6. Singh S., Khulbe KC., Matsuura T, Ramamurthy P. (1998), "Membrane characterization by solute transport and atomic force microscopy", *Journal of Membrane Science*. 142:111-127.

7. Bessieres A., Meireles M., Coratger R., Beauvillain J, Sanchez V. (1996), "Investigations of surface properties of polymer membranes by near field microscopy", *Journal of Membrane Science*, 109:271-284.

8. Huyen Dang.T.T., Amelot C., Rana D., Narbaitz R. M., Matsuura T.. (2010a), "Performance of a newly developed Hydrophilic Additive blended with different ultrafiltration base polymers", *Journal of Applied Polymer Science*, 116(4):2205-2215.

9. Huyen Dang.T.T, Rana D., Narbaitz R. M., Matsuura T. (2010b), "Key Factors Affecting the Manufacture of Hydrophobic Ultrafiltration Membranes for Surface Water Treatment", *Journal of Applied Polymer Science*, 116:2626-2637.

10. Huyen Dang.T.T, Narbaitz R. M., Matsuura T. (2008), "Double-pass casting: A novel technique for developing high performance ultrafiltration membranes", *Journal of Membrane Science*, 323(1):45-52.

11. Anh N.H., Narbaitz R. M., Matsuura T. (2007), "Impacts of Hydrophilic Membrane Additives on the Ultrafiltration of River Water", *Journal of Environmental Engineering*, 133:515-520.

12. Cho J., Sohn J., Choi H., Kim IS, Amy G. (2002), "Effects of molecular weight cutoff, f/k ratio (a hydrodynamic condition), and hydrophobic interactions on natural organic matter rejection and fouling in Membranes", *Journal of Water Supply: Research and Technology-AQUA*. 51(2):109-123.

13. Huyen Dang.T.T. (2009), *Surface modifying macromolecules (SMM)-incorporated UF membranes for natural organic matter removal: characterization and cleaning*. Doctoral thesis. University of Ottawa, Canada.

14. Cho J., Amy G., Pellegrino J. (2000), "Membrane filtration of natural organic matter: comparison of flux decline, NOM rejection, and foulants during filtration with three UF membranes". *Desalination*, 127:283-298.