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Comparison between two Polyethersulfone concentrations in hollow fiber ultrafiltration membranes. Is it worth to use more polymer?

Karen Gonzaga[1+], Jose Carlos Mierzwa[1]

1.University of São Paulo, Engineering, Polytechnic School, Department of Hydraulic and Environmental, São Paulo, São Paulo, Brazil.

+Corresponding author: Karen Gonzaga, **Phone:** +55 11 3039-3273, **Email address:** karen.gonzaga@email.com

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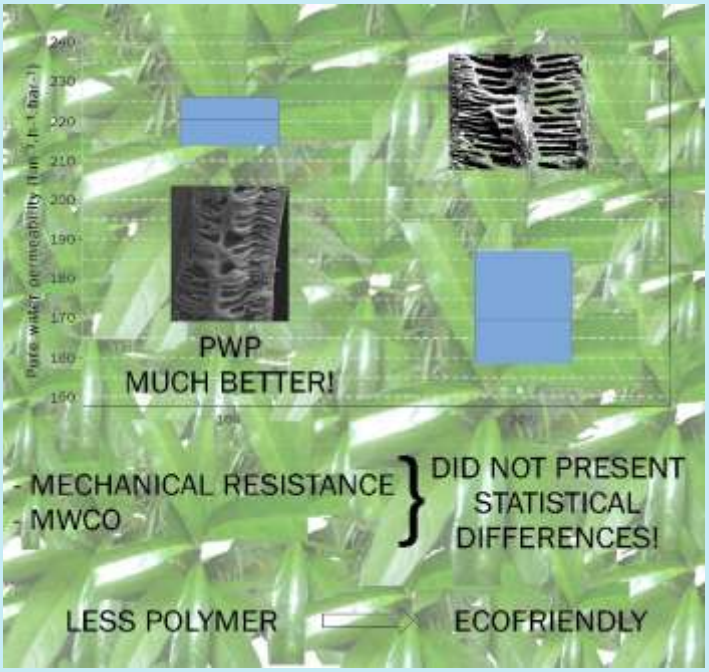
ABSTRACT: Polyethersulfone (PES) hollow fiber membranes were fabricated using dry-jet wet spinning technique, a phase inversion method, with 16 and 20% PES, N-methyl-2-pyrrolidone (NMP) as solvent and tap water as nonsolvent, in order to evaluate if the amount of polymer has a significant effect on its properties. They were characterized using SEM for a morphological analysis, a continuous system to measure pure water permeability (PWP) and molecular weight cutoff (MWCO), and a universal testing machine to tensile tests. The obtained results for PWP was an average of about 220 L m^{-2} h^{-1} bar^{-1} for the 16% PES membrane and 174 L m^{-2} h^{-1} bar^{-1} for the 20% PES membrane. The results of mechanical resistance and MWCO did not present statistical differences. Thus, it is confirmed that the 16% PES membrane can be as good as the 20%, despite using less polymer, a finding that can further motivate membrane modification studies and other related works.



1. Introduction

Polymeric hollow fiber membranes were first developed by Dow Chemical in 1966 and since then, due to their properties as high processability and low cost, they are the most common material used for membrane fabrication[1–3]. Hollow fiber membranes are used in several areas that demand a separation process, such as pharmaceutical industry, food industry, water and wastewater treatment plants and the petroleum sector[4,5].

The method of phase inversion is one of the most important techniques of membrane fabrication[6] for hollow fibers. It is based on an extrusion of a polymer solution through a spinneret, which will return to the solid state[6,7]. Dry-jet wet spinning follows this idea with a phase inversion beginning with an induced evaporation that occurs in the air gap and finishing in the coagulation bath with a phase inversion induced by diffusion[1].

Polyethersulfone (PES) has been widely used because it can tolerate a large range of pH, has a good thermal stability and excellent chemical and mechanical resistance[6,8,9]. This polymer and the conditions for the solution spinning determine the morphology and properties of hollow fiber membrane, such as selectivity[7,10].

Despite numerous studies related to hollow fiber membranes composed of PES[11–16] and the known advantages of membrane separation processes[17–19], there is a worldwide concern with the amount of microplastics that are emerging around the globe[20–23] and not only with energy efficiency, pollutant emissions and other sustainability issues. Lower consumption of plastic is a policy growing in many countries, seeking to encourage consumers to find a way to reduce it on a daily basis[24].

Based on this tendency, the present work focuses on studying the properties of hollow fiber membranes made of 16 and 20% PES, evaluating if there are significant differences among the results obtained that justify the use of a bigger quantity of polymer. Future studies of membrane modification can be based on compositions using smaller amounts of polymer without impairing its application, demonstrating its importance.

2. Experimental

2.1 Materials

Polyethersulfone (VERADEL 3000P with MW = 63,000 g Mol-1) from Solvay Advanced Polymer was dried for 4 h in an oven at 100 °C before utilizing it for fabrication of the dope solution. N-methyl-2-pyrrolidone (NMP) with purity >99% from Labsynth Produtos para Laboratórios Ltda. was used as received as the solvent for the polymer. Tap water was used as the nonsolvent agent, as bore fluid and in coagulation bath.

2.2 Solution preparation

The dope solution was prepared with 16 and 20% (weight/weight) concentration of PES, with the remaining concentration (84 and 80%, respectively) being of NMP. The polymer was slowly added to the solvent, taking 1 h for complete addition, at room temperature. Then, the solution remained for about 18 h at 200 r.p.m. stirring, assuring complete solubilization of the polymer and homogenization, to be finally degassed in an ultrasonic bath for 1 h, eliminating any bubbles of air trapped into solution.

2.3 Hollow fiber production

The solution was spinning with a solution flow rate of 2 mL min^{-1} and a bore fluid flow rate of 4 mL min^{-1}, using dry-jet wet spinning method with an air gap of 2 cm and take-up speed of 4 mL min^{-1}, at room temperature. A schematic representation of the spinneret and fabricating hollow fiber membrane processes is shown in Fig. 1.

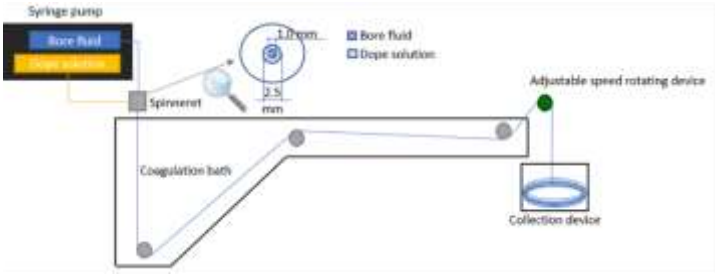


Figure 1. Schematic representation of fabricating hollow fiber membrane system.

Hollow fiber membranes were stored in demineralized water to keep their integrity. To realize some characterization procedures, these were dried following the steps described elsewhere[25].

2.4 Membrane characterization

The produced membranes were investigated about its morphology, permeability, mechanical resistance and MWCO (molecular weight cutoff). The data

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obtained were treated to remove outliers and statistical analysis of the results was done using Minitab® 18.1, from Minitab, Inc., assuming a significance level of 0.05 and equality of variances.

2.4.1 Morphological analysis

The cross-sectional of the hollow fiber membranes was observed by a scanning electron microscope (Zeiss SEM model EVO MA10) with an acceleration voltage of 20 kV. For this, dried membranes were cut under liquid nitrogen and sputter-coated with a thin film of gold-platinum. These procedures under nitrogen are necessary to produce a clean and brittle fracture and the coating is required due to the nature of polymeric material, not electrically conductive. Doing this way, it is possible to see the microstructure of the produced membranes.

2.4.2 Pure water permeability

Pure water permeability (PWP) measurements were estimated in an experimental setup, where a module made from low-density polyethylene (LDPE) was utilized with two hollow fiber membranes with 30 cm effective lengths, folded in half and fed topside in an inside out mode.

A syringe pump with a constant flow rate of 0.5 mL min^{-1} supplied demineralized water to the module and the water production measurement was started after thirty minutes to achieve steady-state conditions. Records were made every five minutes for one hour, similar to the procedure previously described[26]. The permeation flux (J_w) through the membrane was calculated following the Eq. 1:

$$J_w = \frac{V}{A*t*\Delta P} \quad (1)$$

where: J_w = Water permeability (L m^{-2} h^{-1} bar^{-1}); V = Volume of permeate (L); A = Inner surface area (m^{-2}); t = Time (h); ΔP = Transmembrane pressure (bar).

2.4.3 Mechanical resistance

The mechanical resistance of the hollow fiber membranes was investigated by means of tensile tests, measured using an Instron universal testing system and a 100 N load cell and constant rate of 1 mm s^{-1}, with an initial gauge length of 30 mm. The test method was based on ASTM 1557-14 Standard Test Method for Tensile Strength and Young's Modulus of Fibers.

Five dried samples with 100 mm length were tested for each experimental result, determining membrane tensile strength, elongation at break and Young's modulus.

2.4.4 Molecular weight cutoff (MWCO)

The MWCO was investigated using 200 ppm polyethylene glycol (PEG) solution with molecular weights of 10 kDa, 32 kDa, 90 kDa and 150 kDa, into the same system and module described in 2.4.2.

The concentration of PEG in permeate and in retentate was analyzed by a UV-VIS spectrophotometer (WUV-M51, Weblaborsp) at a wavelength of 254 nm and the MWCO was determined from the rejection of PEG solution, following Eq. 2:

$$\boldsymbol{R = \left(1 - \frac{C_p}{C_r}\right) * 100\%} \quad (2)$$

where: R = Rejection (%); C_p = Permeate concentration (Da); C_r = Retentate concentration (Da).

3. Results and discussion

3.1 Morphological analysis

To evaluate the impact of polymer concentration on the morphology of hollow fiber membranes, SEM was used to observe its enlarged cross section and outside face of the samples. Figures 2 and 3 show both membranes resulted in an outside dense skin and a double layered finger-like structure pore, but it is possible to see that the 16% PES concentration membrane has a bigger aperture at the end of the pores, nearby their center.

Double layer finger-like and dense skin were expected microstructure characteristics for these membranes. They occur because water is a strong nonsolvent for the polymer, that provides a fast coagulation, and this formation is a consequence of it, like reported previously[11,27,28].

The morphological analysis indicates that the permeation flux tends to be better in the 16% PES concentration membrane. This tendency is verified by pure water permeability investigation results, but it can happen because its pores had an opening larger than the other membrane, facilitating the flow of the fluid through it.

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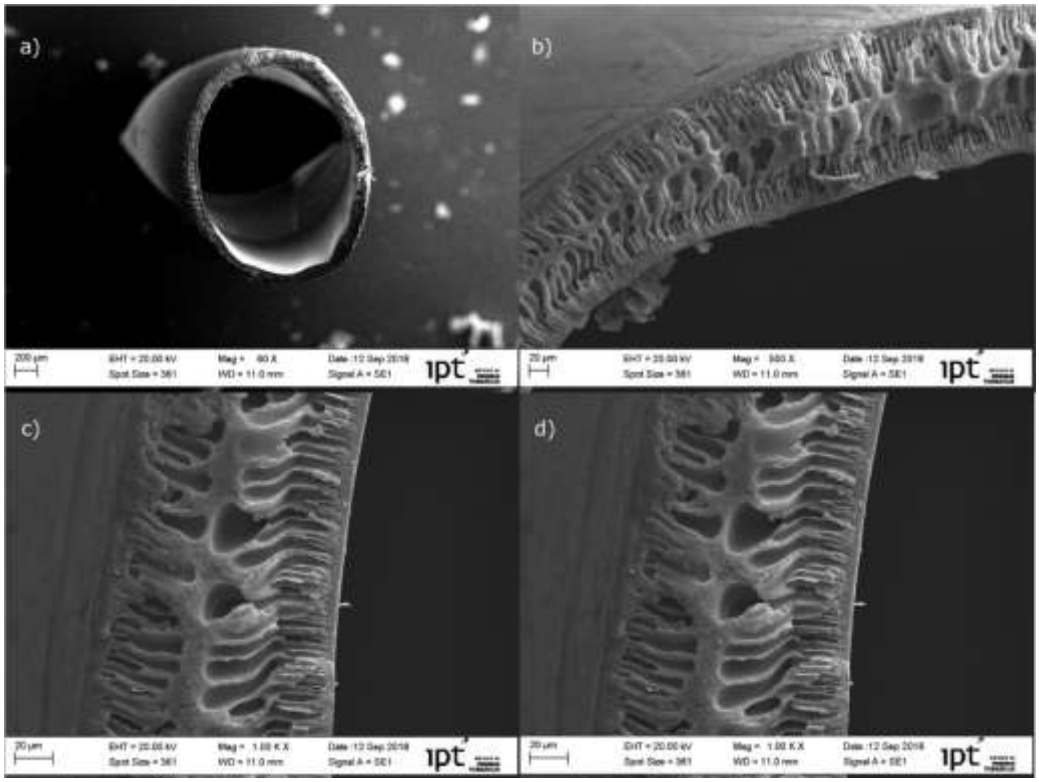

Figure 2. SEM images of 16% PES sample: a) full cross section of the hollow fiber membrane, b) and c) cross section of the hollow fiber membrane with different magnifications, and d) outer skin.

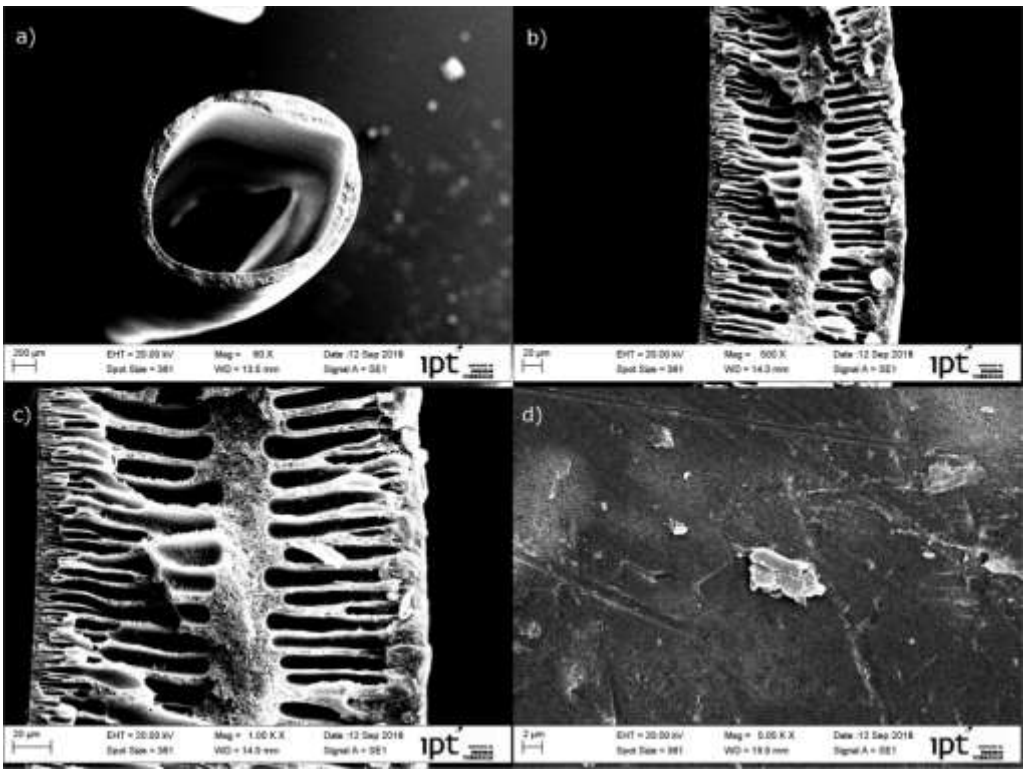

Figure 3. SEM images of 20% PES sample: a) full cross section of the hollow fiber membrane, b) and c) cross section of the hollow fiber membrane with different magnifications, and d) outer skin.

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3.2 Pure water permeability

The results of demineralized water permeation flux for the hollow fiber membranes produced are shown in Fig. 4. It shows an average permeability about 220 L m^{-2} h^{-1} bar^{-1} for the 16% PES concentration membrane and 174 L m^{-2} h^{-1} bar^{-1} for the 20% PES concentration membrane. These results agree with the SEM analysis showed above and also with reports in the literature[29,30].

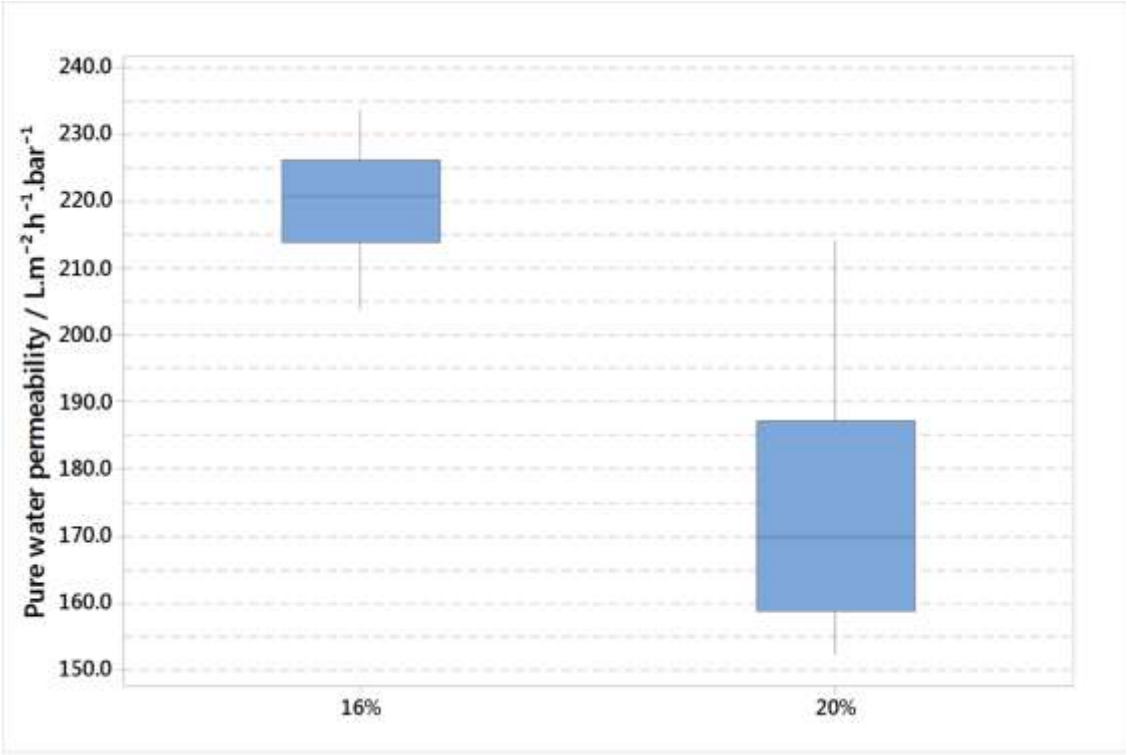

Figure 4. Pure water permeability of 16% PES and 20% PES membranes.

Table 1 shows statistical analysis of the results of permeability presented. According to ANOVA evaluation, there is a statistical difference between them.

Table 1. ANOVA statistical analysis of membranes PWP.

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Factor	1	12208	12207.90	56.11	0.000
Error	22	4787	217.60		
Total	23	16995			

3.3 Mechanical resistance

The results of the mechanical properties investigation for membranes are summarized in Tab. 2.

Table 2. Mechanical resistance properties of membranes.

Sample	Tensile strength / MPa		Elongation at break / %		Young's Modulus / MPa	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
16%	220	9	15	2	180	47
20%	174	19	15	2	279	54

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These results show there is a small variance between the average of tensile strength, elongation at break and Young's modulus. With the analysis of results, it is possible to note there is no relevant difference between the 16 and 20% PES membranes (Tabs. 3 to 5).

Table 3. ANOVA statistical analysis of membranes tensile strength.

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Factor	1	0.0918	0.09177	0.02	0.884
Error	7	28.0531	4.00759		
Total	8	28.1449			

Table 4. ANOVA statistical analysis of membranes elongation at break.

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Factor	1	167.6	167.6	1.18	0.339
Error	4	568.8	142.2		
Total	5	736.4			

Table 5. ANOVA statistical analysis of membranes Young's Modulus.

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Factor	1	14656	14656	5.73	0.075
Error	4	10235	2559		
Total	5	24891			

3.4 MWCO

The data obtained for MWCO were recorded up to PEG 150 kDa MW and the membranes were not able to remove 90% of this substance, which is the concept of MWCO. Thus, to estimate this important characteristic of membranes and knowing that the typical rejection curve is sigmoidal[31,32], an extrapolation was made with the results (Fig. 5 and 6).

Based on the point that represents 90% of removal in these curves, values of 271 kDa and 279 kDa are the MWCO estimated of 16% PES membrane and 20% PES membrane, respectively. The statistical analysis does not show a relevant difference between both results, as demonstrated in Tab. 6.

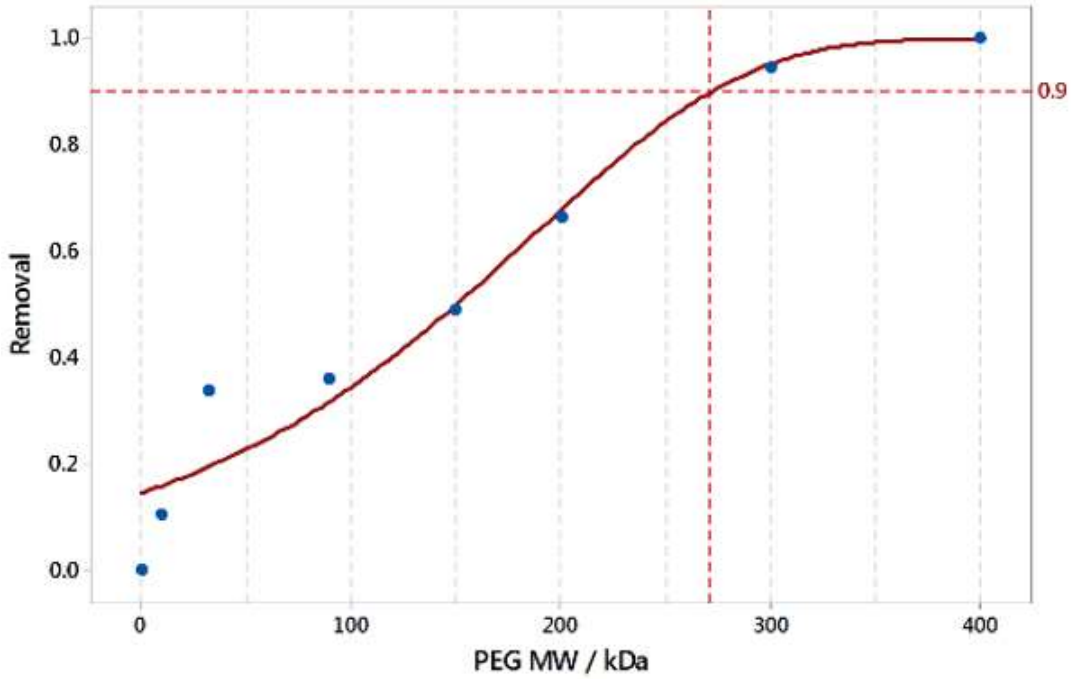

Figure 5. 16% PES membrane MWCO.

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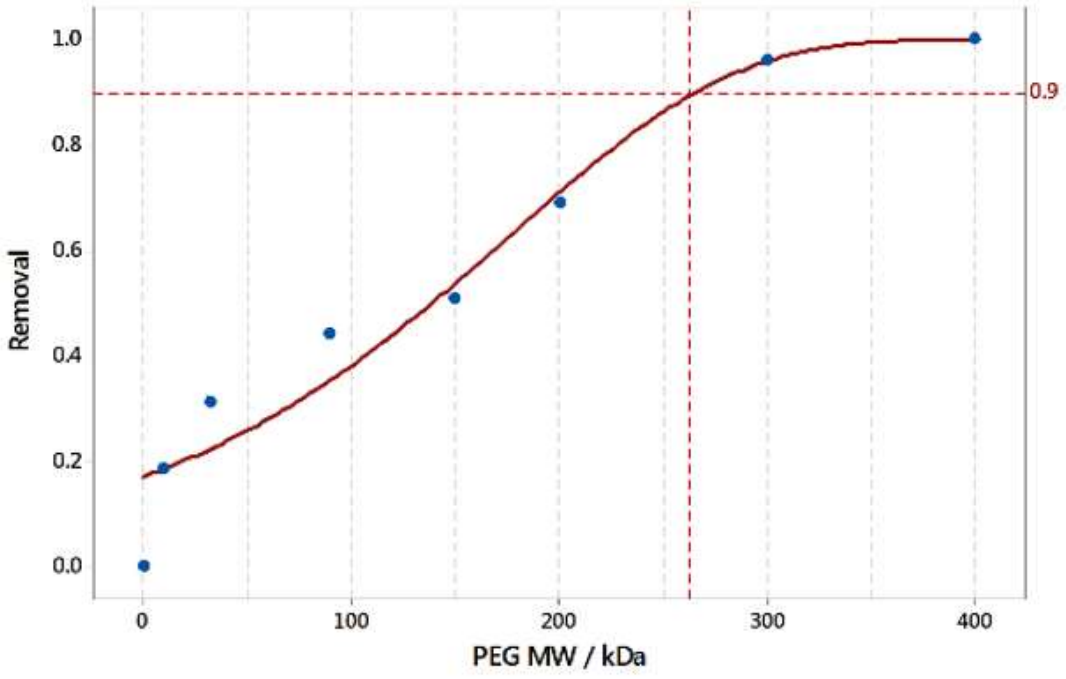

Figure 6. 20% PES membrane MWCO.

Table 6. ANOVA statistical analysis of membranes MWCO.

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Factor	1	0.00238	0.002377	0.02	0.894
Error	14	1.81083	0.129345		
Total	15	1.81320			

4. Conclusions

In this work, 16 and 20% PES membranes were compared to verify whether the concentration of polymer can determine a significant difference between them. Based on results obtained, it is possible to observe that the only relevant statistical difference was PWP, which is almost 25% better in the 16% PES membrane, implying a minor energy consumption to produce the same volume of permeate compared to the 20% PES. All other results have no relevant statistical difference among the compared membranes.

Future studies involving membrane modification can benefit from this research and motivate researchers to develop other works with related themes.

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