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Research Paper

Glycerin Removal from Ultrafiltration Flat Sheet Membranes by Filtration and Soaking

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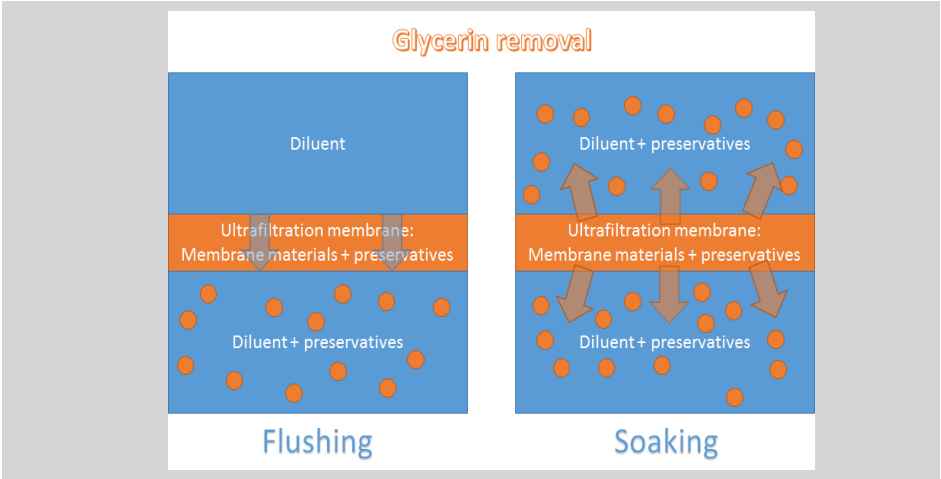
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Quantification of glycerin removal from membranes: Membrane and supplier screening
- Comparison of removal processes: soaking (diffusion) vs flushing (filtration)
- Effect of operating parameters: flowrate vs exposure time

ABSTRACT

In the case of pharmaceutical processes, the presence of preservatives can be problematic and the quantity is subject to stringent standards. So, the aim of this study is to quantify the removal of glycerin contained in ultrafiltration flat sheet membranes by filtration and soaking. This is carried out over a wide range of membranes with different characteristics. The selected flat sheet membranes (with a surface of 14.5 cm²) have a Molecular Weight Cut-Off (MWCO) ranging from 5 to 60 kDa. They are made of different organic materials (polyethersulfone, regenerated cellulose and etc.) and are manufactured by different suppliers (Millipore, Sartorius, GE Osmonics, Novasep, Pall). The density and therefore the glycerin concentration measurements are carried out in filtered distilled water (dead-end filtration) and distilled water of soaking (diffusion phenomenon). This study gives experimental information about the glycerin quantity as a function of membrane characteristics and the position of glycerin on the membrane (skin layer and support). The various studied parameters are the removal kinetic, the filtered volume, the filtration pressure and the contact time.

1. Introduction

The presence of preservatives in organic membranes is necessary whatever the membrane material to maintain open pores and to preserve the membrane before use. Furthermore, these preservatives make the surface as hydrophilic as possible (vs. material used). Preservatives quantities differ among all the existing ultrafiltration flat sheet membranes. However, in some industrial processes and particularly in the pharmaceutical production, the preservative quantity is specified by stringent standards and must be monitored.

The membrane conditioning depends on suppliers/manufacturers and more particularly on membrane characteristics; such as MWCO, material, thickness and permeability. The preservative removal procedures depend on suppliers in terms of time and volume process using acid, basic or distilled water rinsing. The membrane rinsing procedures are given as recommendations and are generally provided by the supplier in the documentation. However, the rinsing process and its operating conditions should be determined by the end user as it depends on the membrane material and its application. This includes, for example, basic rinsing to regenerated cellulose membranes [1,2], acid rinsing to acetate membranes [3] or distilled

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water rinsing [4] for different operating conditions [3].

Furthermore, the nature of chemical compounds is not explicitly reported in the literature and depends on suppliers [5]. The most commonly used are: glycerin (Koch Membrane Systems, Millipore, Sartorius and etc.), sodium azide (Millipore) and distilled water-alcohol mixture (GE Healthcare). But, few information are available about their initial quantities.

It appears that the membrane characteristics, such as pore volume and thickness play an important role in the initial quantity [6]. Indeed, the higher the pore volume is, the higher the preservative quantity in the membrane is. This is also linked to the membrane thickness because Wright et al. shows that, when thickness is important, the preservative quantity removed is high. The use of a low flow leads to more contact time, which it promotes the preservative removal [6]. This work approaches to the development of drug production process, for example the treatment of cystic fibrosis. This genetic disease is responsible for thickening of the mucus (difficult to expectorate) and leads to successive respiratory infections. Treatment consists of daily administrations to limit these bacterial infections. Daily administration (10 mL) of the drug, after *in situ* production and purification by membrane can offset the weak immune system. Therefore, the glycerin quantity in each administration must be limited to avoid accumulation in the lungs. For this type of production, it is necessary to quantify the initial glycerin quantity.

The aim of this work is to evaluate the importance of operating parameters that can influence the glycerin removal, such as the filtered and soaked distilled water volume, the filtration pressure and the contact time on a wide range of ultrafiltration flat sheet membranes. The purpose is to use the membrane for pharmaceutical applications (low UF process). The experimental study of the glycerin position and quantity was realized here with the density measure developed procedure.

2. Experimental

2.1. Materials

Table 1 shows the ultrafiltration membranes tested in this work. The membranes were selected from five different suppliers, including GE Osmonics, Sartorius, Millipore, Pall and Novasep, and made of different materials (i.e. polyethersulfone, regenerated cellulose, PVDF, and polysulfone). These membranes also are different in thickness (see Table 1) and therefore in their pore volumes. All membranes were stored at room temperature (20°C ± 2°C) before they used for experiments.

The experimental system used in this work is a dead-end filtration cell (50 mL) with a 14.5 cm² membrane surface, which presented in Figure 1. The constant applied pressure is 2 bar. To test the glycerine removal efficiency, 100 mL of distilled water is filtered and then 10 mL of permeate is analysed with a densimeter to determine the glycerin concentration and to plot the removal kinetic.

During soaking, the membrane samples were fully immersed in 10 mL of distilled water in a petri dish (5 cm of diameter) for 24 hours, with or without renewal of distilled water. So, the glycerin quantity contained in the flat sheet membrane is determined by soaking and compared to the glycerin quantity obtained by filtration. For the two 10 kDa polyethersulfone (PES) membranes (supplied from Sartorius and Millipore), the membranes were fully immersed in 10 mL of distilled water in a petri dish in a range of 20 seconds up to 24 hours, to observe more precisely the effect of contact time on the glycerin removal. The soaking volume of 10 mL is required so that the membrane is fully immersed in the solvent. All experiences were carried out at room temperature (20°C ±2°C).

2.2. Position of glycerin in the membrane

To study the glycerin position, an ultrafiltration cell with two parts (thefeed support and the permeate support) was equipped with a flat sheet membrane (14.5 cm²) and used (Vivaflow system from Sartorius supplier (see Figure 2)). The liquid was introduced by a syringe pump to the module and then three samples of 3 mL were successively recovered in the retentate followed by three samples of 3 mL recovered in the permeate. The membrane was used right side up and upside down to determine where a greater glycerin quantity is located in the membrane's structure, i.e. skin layer or support. These experiments were carried out using two 10 kDa membranes made of PES and supplied from Sartorius and Millipore.

2.3. Densimeter analysis

A high precision densimeter is used to study the glycerin quantity in all the membranes presented in Table 1. The DMA 5000M was used in this work, which has a manufacturer quoted precision of 0,000005 g.m^{-3}. New densimeter methodology has been developed to determine the glycerin quantity [References: air density = 0,001192 g.cm^{-3} at 20°C and distilled water density = 0,998192 g.cm^{-3} at 20 °C]. Prior to each sample measurement, a distilled water reference measurement was carried out to verify the device reliability. The determination of glycerin concentration was made with a calibration curve and the experimental densimeter detection limit is 0.1 mg.mL^{-1} (about 0.07 mg.cm^{-2}).

Table 1
Tested membranes characteristics (material, MWCO, permeability and thickness).

Supplier	Material	MWCO (kDa)	Permeability (L.h^{-1}.m^{-2}.bar^{-1})	Thickness (µm)	Reference
GE Osmonics	PS[1]	60	NA	NA	YMEWSP3001
GE Osmonics	PS	30	NA	NA	YMERSP3001
GE Osmonics	PVDF[2]	30	NA	NA	YMJWSP3001
GE Osmonics	CA[3]	20	NA	NA	YMCQSP3001
GE Osmonics	PES[4]	10	NA	152-177	YMPWSP3001
Sartorius	RC[5]	30	140	120	14459-47------D
Sartorius	RC	10	60	120	14439-47------D
Sartorius	RC	5	20	120	14429-47------D
Sartorius	PES	50	600	120	14650-47------D
Sartorius	PES	30	270	120	14659-47------D
Sartorius	PES	10	170	120	14639-47------D
Sartorius	PES	5	20	120	14629-47------D
Millipore Ultracel	RC	10	61	130	PLCGC10205
Millipore Biomax	PES	50	689	280	PBQK50205
Millipore Biomax	PES	30	544	280	PBTK04710
Millipore Biomax	PES	10	392	280	PBGC10205
Pall Oméga	PES	10	NA	NA	OM010043
Novasep	PES	10	200	NA	PP010SR05

[1]*PS: polysulfone*
[2]*PVDF: polyvinylidene fluoride*
[3]*CA: cellulose acetate*
[4]*PES: polyethersulfone*
[5]*RC: regenerated cellulose*

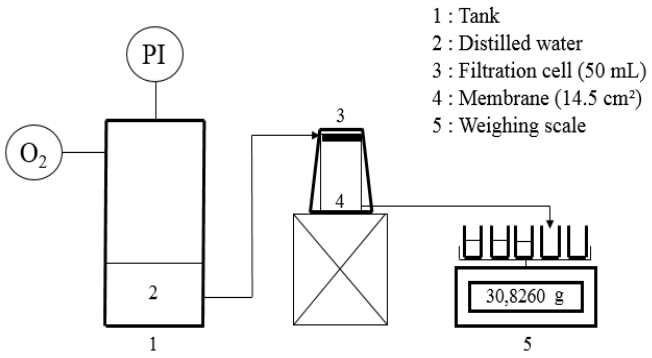

Fig. 1. Dead-end filtration process.

3. Results and discussion

3.1. Glycerin position on the membrane

Before examining the effect of each parameter (supplier, MWCO, material, filtration pressure and contact time) on glycerin removal for all the

tested membranes, the glycerin position on the membrane, i.e. skin layer or support, was studied.

Table 2 shows that the removed glycerin quantity is higher when the feed is placed on the skin of the membrane compared to the glycerin quantity obtained when the distilled water is fed on the membrane support (upside down) for two tested membrane samples (i.e. Millipore and Sartorius, made of PES, 10 kDa). This indicates that a greater glycerin quantity is contained on the membrane separating layer compared to the support layer. This can be concluded that the fact is true for all membranes tested (Sartorius membrane is 120 µm thick and Millipore membrane is 280 µm thick (see Table 3)).

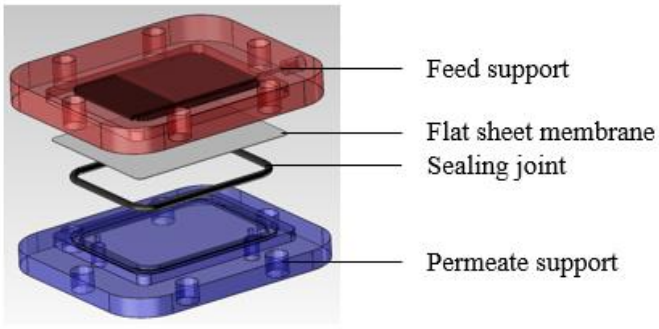

Fig. 2. System to study the position of glycerin in the ultrafiltration flat sheet membrane.

For the membrane sample supplied from Millipore (using right side up mode), the total glycerin quantity removed by soaking is 4.4 mg.cm^{-2} (retentate) and 1.3 mg.cm^{-2} additional (permeate) by filtration, while using upside down mode, the total quantity removed by soaking is 0.05 mg.cm^{-2} and 4.3 mg.cm^{-2} by filtration. Consequently, this indicates that the majority of glycerin is located on the skin of the membrane with a minimal quantity on the membrane support. Moreover, the porosity is more important than the separating layer.

For the membrane sample supplied by Sartorius (using right side up mode), the total glycerin quantity removed by soaking is 3.2 mg.cm^{-2} and 2.6 mg.cm^{-2} by filtration, while using upside down mode, the total quantity removed by soaking is 4.2 mg.cm^{-2} and 1.0 mg.cm^{-2} by filtration. As could be observed, the difference between the values obtained at the retentate and at the permeate for the membrane sample from Sartorius is smaller. This can be explained by a more homogenous distribution of glycerin within the membrane (skin and support layers) compared to the Millipore membrane.

Comparative results of the three methodologies used in this work, i.e. soaking-filtration, filtration and soaking over a period of 24 hours, are presented in Table 3. As could be observed, glycerin removal is improved by the diffusion phenomenon (contact time). Indeed, the difference between the results obtained using soaking-filtration (3×3 mL, 3×3 mL) and one soaking (10 mL) of Millipore membrane show that soaking followed by filtration is more effective than a simple soaking procedure, with a total glycerin quantity removed of 5.8 mg.cm^{-2} versus 4.9 mg.cm^{-2}, respectively. This may be due to this fact that the glycerin is not uniformly distributed with a greater quantity on the membrane separating layer and a minimal quantity on the membrane support. While for Sartorius membrane, a more homogeneous distribution would explain the lower difference between the values of 5.9 mg.cm^{-2} with the soaking-filtration process and 5.7 mg.cm^{-2} with a single soaking. It is important to note that the quantity of removed glycerin by filtration is lower than that by soaking. This can be translated to this fact that the diffusion phenomenon is more important than that of the filtered volume.

3.2. Influence of suppliers/manufacturers on glycerin removal for PES membrane (MWCO = 10 kDa)

The initial glycerin quantity contained in the ultrafiltration flat sheet membranes could be different according to the supplier. Indeed, even for different batches of the same membrane, for instance the Millipore, the membrane thickness can vary from 240 to 350 µm with an average thickness of 280 µm. This can induce a variation of the initial glycerin quantity.

Figure 3 clearly shows that the removed glycerin quantity varies between membrane suppliers, eve with the same material and the MWCO value. These values are also compared in Table 3. This can be explained by the membrane constitution (e.g. thickness and pore volume) that can influence the diffusion, and therefore directly impact the glycerin removal. Furthermore, a similar pattern of the quantity of glycerin removal by filtration is obtained: 4.3 mg.cm^{-2} for Sartorius, 3.5 mg.cm^{-2} for Millipore, 2.8 mg.cm^{-2} for Pall, 2.2 mg.cm^{-2} for Novasep and 0.7 mg.cm^{-2} for GE Osmonics, respectively. These values are linked to the membrane permeabilities. In better words, it seems that a greater glycerin quantity is removed where the membrane permeability is higher. Moreover, these quantities are always lower than the glycerin quantity removed by soaking. Apparently, the lower the membrane thickness is, the higher is the glycerin quantity removed (Sartorius membrane: 120 µm and Millipore membrane: 280 µm). On the other hand, The initial quantity of glycerin depends on the membrane supplier for a same material and MWCO (PES, 10 kDa) in the following order: Sartorius > Millipore > Pall > Novasep > GE Osmonics.

3.3. MWCO influence on glycerin removal

The influence of MWCO on glycerin removal was studied for two suppliers, Sartorius and Millipore and for a same membrane material, i.e. PES. Figure 4 shows that the higher the MWCO is, the higher the glycerin quantity removed by soaking is. This can be attributed to the greater pore volume associated with higher MWCO [6]. This is true whether the glycerin is uniformly distributed (Sartorius membranes) or not (Millipore membranes).

By filtration, for the Millipore membranes, in the first 10 mL filtered, the glycerin quantity removed is 3.7, 2.6 and 2.5 mg.cm^{-2} and the final quantity, after filtering by 100 mL, is 3.9, 3.4, 3.2 mg.cm^{-2} for 50-30-10 kDa membranes, respectively (see Figure 5a). Figure 5a shows that, for 30 and 10 kDa membranes, about 75% of the total glycerin content (removed by filtration) is extracted during the first 10 mL filtered. Afterward, the glycerin removal is progressive. For the 50 kDa MWCO membrane, there is a very low variation of the removal kinetic after the first 10 mL filtered, where 95% of the total glycerine content removed, is extracted. For Millipore membranes, the majority of glycerin is located on the membrane separating layer, so, the use of a greater pore volume will improve the removal (see Figure 5a).

Table 2
Glycerin quantity removed (mg.cm^{-2}) as a function of soaked and filtered distilled water volume, right side up and upside down membrane [Millipore-Sartorius, PES, 10 kDa, V = 9-9 mL, S = 14.5 cm²].

Membrane	Way	Mass (g)	Time (minute)	Source	Glycerin quantity removed (mg.cm^{-2})	Total glycerin quantity removed (mg.cm^{-2})
Millipore PES 10	Right side up	10	4	retentate	4.4	5.8
		10.1		permeate	1.3	
	Upside down	9.2	6	retentate	0.05	4.3
		9.8		permeate	4.3	
Sartorius PES 10	Right side up	9.4	5	retentate	3.2	5.9
		9.5		permeate	2.6	
	Upside down	10.1	5	retentate	4.2	5.3
		9.5		permeate	1.0	

Table 3
Glycerin quantity removed (mg.cm^{-2}) by filtration and by soaking of distilled water as a function of membrane suppliers and membrane characteristics (material, MWCO, permeability and thickness).

Supplier	Material	MWCO (kDa)	Permeability (L.h^{-1}.m^{-2}.bar^{-1})	Total glycerin quantity removed (mg.cm^{-2})	
				Filtration (2bar)	Soaking (24 hours)
GE Osmonics	PS	60	NA	1.6	1.9
GE Osmonics	PS	30	NA	1.2	1.8
GE Osmonics	PVDF	30	NA	1.5	2.2
GE Osmonics	CA	20	NA	2.8	3.2
GE Osmonics	PES	10	NA	0.7	1.5
Sartorius	RC	30	140	7.0	9.7
Sartorius	RC	10	60	5.1	6.2
Sartorius	RC	5	20	5.5	5.2
Sartorius	PES	50	600	2.0	6.1
Sartorius	PES	30	270	3.2	6.0
Sartorius	PES	10	170	4.3	5.7
Sartorius	PES	5	20	4.1[1]	5.2
Millipore Ultracel	RC	10	61	2.8	3.5
Millipore Biomax	PES	50	689	3.9	5.8
Millipore Biomax	PES	30	544	3.7	5.4
Millipore Biomax	PES	10	392	3.5	4.9
Pall Oméga	PES	10	NA	2.8	2.5
Novasep	PES	10	200	2.2	2.8

For Sartorius membranes, Figure 5b shows that the tendency is reversed compared to Millipore membranes. In better words, the higher the MWCO is, the lower the glycerin removal by filtration is. In this case we experienced that the glycerin content removed after the first 10 mL filtered are 1.7, 3.1, 3.3 and 3.6 mg.cm^{-2} for 50-30-10-5 kDa membranes, respectively. Moreover, the final quantity removed, after 100 mL filtered, are 2.1, 3.2, 4.3 and 4.1 mg.cm^{-2} for 50-30-10-5 kDa membranes, respectively (see Figure 5b). To explain and confirm this difference, the membrane permeabilities were examined. Indeed, with the Sartorius membranes, the variation of the filtration time, and therefore, the contact time is more important among 50 kDa (600 L.h^{-1}.m^{-2}.bar^{-1}), 30 kDa (270 L.h^{-1}.m^{-2}.bar^{-1}), 10 kDa (170 L.h^{-1}.m^{-2}.bar^{-1}) and 5kDa (20 L.h^{-1}.m^{-2}.bar^{-1}) samples, compared to the Millipore membranes (permeability > 400 L.h^{-1}.m^{-2}.bar^{-1} whatever MWCO) (see Table 3).

3.4. Influence of membrane material on glycerin removal

It can be concluded that the results follow the same tendency with both suppliers where the majority of glycerin is located in the membrane surface. In better words, the glycerin quantity removed is higher by soaking compared to filtration and for the membranes with higher MWCO. This is true by soaking, however, by filtration, the quantity removed is not only a function of membranes' MWCO. This means that if permeability is similar for different MWCO, the conclusion is similar. But, if permeability is strongly different and for a similar volume of permeate, so the contact time appears as a controlled parameter.

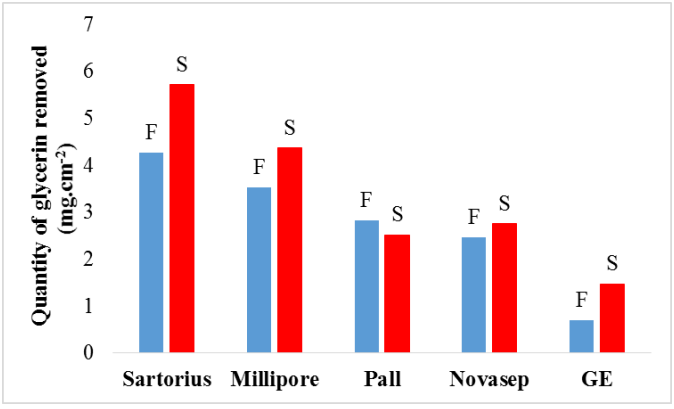

Fig. 3. Variation of glycerin quantity removed (mg.cm^{-2}) by filtration F and by soaking S as a function of different PES 10 kDa membrane suppliers.

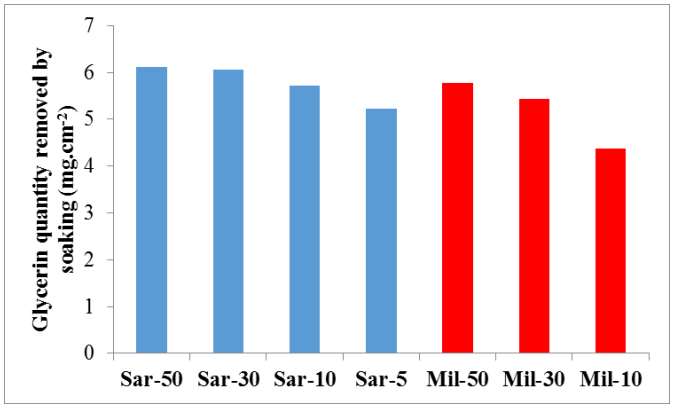

Fig. 4. Variation of glycerin quantity removed (mg.cm^{-2}) by soaking in PES membrane as a function of MWCO [50-30-10-5 kDa] and membrane suppliers [Sartorius-Millipore].

The membrane material is an important parameter that directly influences the initial glycerin quantity on the membrane. Indeed, the glycerin quantity varies according to the material hydrophobicity. Two materials are mainly investigated in this work, including PES and regenerated cellulose (RC). The comparison between membrane materials was carried out based on membranes from the same supplier, i.e. Sartorius, with the same thickness, i.e. 120 µm, and for 30, 10 and 5 kDa MWCO membranes.

The results presented in Table 3 show that the RC membranes contained more glycerin than that of PES membranes, whatever the protocol for removal is. This can be explained by the fact that the material is less hydrophilic (and therefore requires a greater glycerin quantity).

However, it is impossible to compare the removed quantity between the different MWCO (30,10 and5 kDa) because the contact time is very different with about 8 minutes for high MWCO membrane and 5 hours for low MWCO one. For other materials, the comparison is difficult, because other parameters vary in tandem with this: the MWCO for GE Osmonics membranes and the permeability (factor 6) for Millipore membranes (RC-PES membrane with a MWCO of 10 kDa).

3.5. Effect of the transmembrane pressure

The filtration pressure can affect the removed glycerin quantity. Indeed, according to the supplier, the extracted quantity varies as a function of the applied pressure for the filtration process.

Figure 6 presents the results obtained with the Novasep membrane at 1, 2 and 3 bars. It is observed that when the pressure is lower, the glycerine removal is better. In better words, for 1 bar applied pressure a final glycerin quantity removed was measured at 2.4 mg.cm^{-2}, while for 2 bar the same value was measured at 2.2 mg.cm^{-2}. It is worth quoting that the removed glycerine was also measure at 1.9 mg.cm^{-2} for 3 bar applied operating pressure. So, it can be concluded that the increase in filtration time (or contact time), at low transmembrane pressure, improves the glycerin removal.

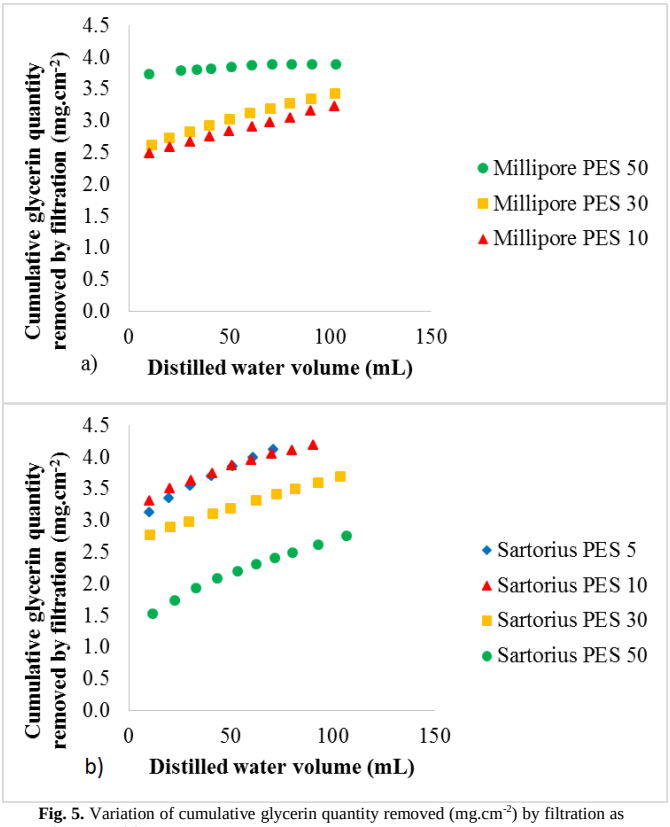

Fig. 5. Variation of cumulative glycerin quantity removed (mg.cm^{-2}) by filtration as a function of filtered distilled water volume (mL):
a) [Millipore, 50-30-10 kDa, PES, P = 2 bar, S = 14.5 cm²]
b) [Sartorius, 50-30-10-5 kDa, PES, P = 2 bar, S = 14.5 cm²]

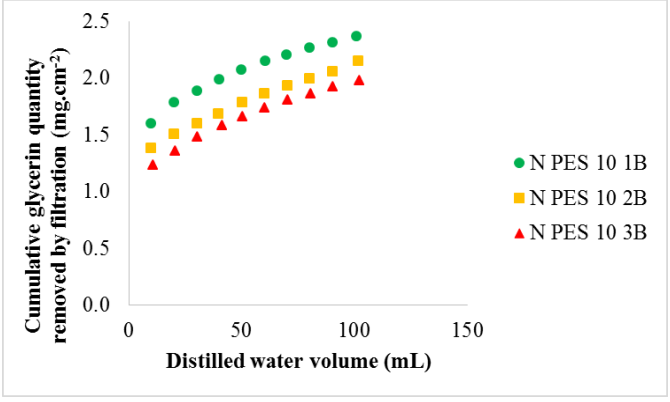

Fig. 6. Variation of cumulative glycerin quantity removed (mg.cm^{-2}) by filtration as a function of filtered distilled water volume [Novasep, PES, 10 kDa, P = 1-2-3 bar, S = 14.5 cm²].

Table 4 shows that the glycerin removal depends on the transmembrane pressure. When the initial quantity is lower, the influence of the transmembrane pressure and therefore the contact time is less, significantly. So, it is with Novasep and Pall membranes with a glycerin quantity removal less than 3 mg.cm^{-2}, whatever the transmembrane pressure is and the methodology used, compared to Sartorius and Millipore membranes.

Based on the obtained results, this can be concluded that the applied pressure is not the most important parameter on glycerin removal, it is rather the contact time. In the model of Wright et al. [6], this parameter is not taken into account. In fact, the total mass/area of humectant permeated over time Mt (g.cm^{-2}) is related to the total volume/area permeated Vp (cm^3.cm^{-2}) by the following equation:

$$M_t = M_\infty \left[1 - \exp\left(-\frac{V_p}{l}\right) - \frac{V_p}{l\theta}\exp\left(-\frac{V_p}{l\theta}\right)\right] \quad (1)$$

where M_∞ is a fitting constant related to the total amount of TOC released (g.cm^{-2}), and θ is another fitting parameter. Each V hypothetical volume has a characteristic length (cm).

A good agreement is observed between the mentioned model (see Ref. [6]) and our results (see Figure 7) with significant values of the fitting constant. However, this value is only true for a transmembrane pressure of 2 bars. For other transmembrane pressures and with the same membrane, the fitting constants will be modified. The model is not easy because the contact time will be taken into account.

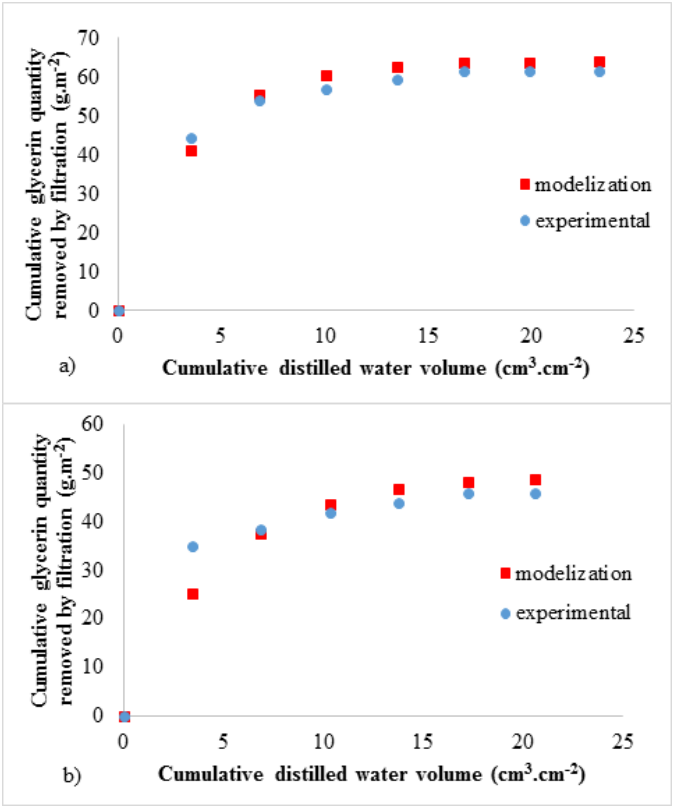

Fig. 7. Variation of cumulative glycerin quantity removed by filtration (g.m^{-2}) as a function of cumulative filtered volume (cm^3.cm^{-2}) obtained by modelization and experimentally
a) Sartorius membrane, PES, 10 kDa [M∞ = 50 mg; V_{total} = 330 mL; l = 3,4264, θ = 0,0048]
b) Millipore membrane, PES, 10 kDa [M∞ = 64 mg; V_{total} = 500 mL; l = 4,8625, θ = 0,0048].

3.6. Influence of the contact time

To conclude that the contact time is the most important parameter on the glycerin removal, all the membranes were studied after a 24-hour soaking in 10 mL of distilled water (see Figure 8). These results presented as a function of membrane's MWCO, and show a large dispersion for different membranes (both suppliers and materials). The variation of the contact time, between 20 seconds and 24 hours, was studied more precisely with two PES membranes (MWCO: 10 kDa), supplied from Sartorius and Millipore. It is worth quoting that, here, only the diffusion phenomenon was studied.

The results presented in Figure 9 show that the glycerin quantity removed from the Sartorius membranes is constant at about 6.2-6.6 mg.cm^{-2}. For a contact time below 2 minutes, it is too short to remove glycerin completely with only one soaking because only 90% of glycerin is removed (5.4 mg.cm^{-2} in 45 seconds), compared to 6.2 mg.cm^{-2} in 2 minutes. Figure 9 shows clearly this stabilisation at 2 minutes. However, successive soakings are made and the results indicate an improvement of glycerin removal. Indeed, at four

successive soakings (3 successive soakings of 10 mL for 2 minutes and 1 soaking of 10 mL for 24 hours), the total glycerin quantity removed of 6.6 mg.cm^{-2} is more important than one soaking (around 6.2 mg.cm^{-2}). In this case, the number of successive soaking is only limited by the detection limit of densimeter at 0.1 mg.mL^{-1} (0.07 mg.cm^{-2}).

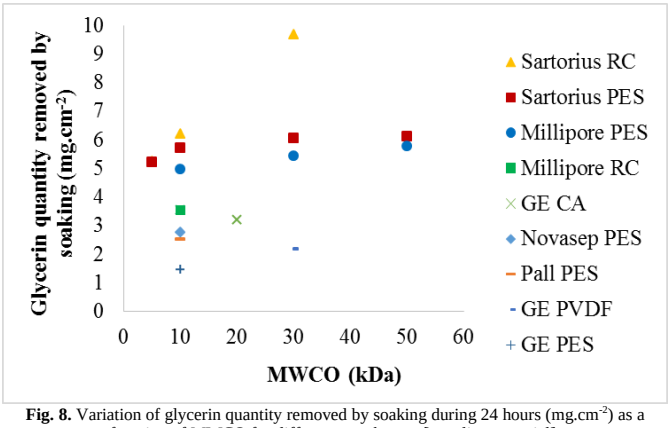

Fig. 8. Variation of glycerin quantity removed by soaking during 24 hours (mg.cm^{-2}) as a function of MWCO for different membranes [supplier, material].

Table 4
Comparison of the results by filtration and by soaking as a function of PES 10 kDa membrane suppliers and filtration pressure.

Supplier	Filtration		Soaking 24 hours
	Pressure (bar)	Total glycerin quantity (mg.cm^{-2})	Total glycerin quantity (mg.cm^{-2})
Novasep	3	1.98	2.75
	2	2.15	
	1	2.37	
Pall	3	2.13	2.51
	2	2.18	
	1	2.19	
Sartorius	3	5.17	5.72
	2	4.26	
	0.6	3.52	
Millipore	3	3.92	4.97
	2	3.53	
	1	3.48	
	0.6	2.78	

The results obtained for Millipore membranes are similar to those obtained for Sartorius membranes with a minimum soaking time of 5 minutes. This longer time may be explained by a less homogeneous distribution compared to Sartorius membranes. This is observed with successive soakings where glycerin removal is improved. However, this difference is not significant. The results for the Millipore membrane show that between 5 minutes and 24 hours, the glycerin quantity removed is almost similar (4.9-5.2 mg.cm^{-2}). But, below 3 minutes, the contacting time is too short to remove the glycerine, completely (4.7 mg.cm^{-2}, i.e. <90%). Furthermore, it is important to note the difficulty to obtain a total removal by the filtration process, but it seems feasible with the soaking process. Indeed, in the case of this Millipore membrane, the maximal glycerin quantity removed by filtration is 3.5 mg.cm^{-2} in 8 minutes (100 mL), while the value obtained by soaking is 4.9 mg.cm^{-2} (after 2 minutes of soaking, 10 mL) (see Table 3).

All the obtained results show that the contact time and, therefore, the diffusion phenomenon are the most important parameters for glycerin removal from ultrafiltration flat sheet membranes. For this reason, the filtration process removes less glycerin than the soaking process due to the short filtration time, i.e. less than 5 minutes. Indeed, soaking requires a small volume of distilled water, for example 10 mL in 3-4 minutes, to remove 90% of the total extracted glycerin. To remove the remained 10%, the soaking volume can be changed. The soaking in the distilled water is the only way to totally remove the glycerin.

3.7. Influence of batch production

The membrane conditioning is a function of supplier/manufacturer. Different tests were performed with different batches (see Figure 10). For a same supplier and a same membrane (PES, 10 kDa), the glycerin quantity can vary from one batch to another. Indeed, the results presented in Figure 10 show that there is a high heterogeneity between batches and suppliers. For instance, variation on glycerin quantity removed is not significant for Millipore but it is significant for Sartorius and Novasep membranes.

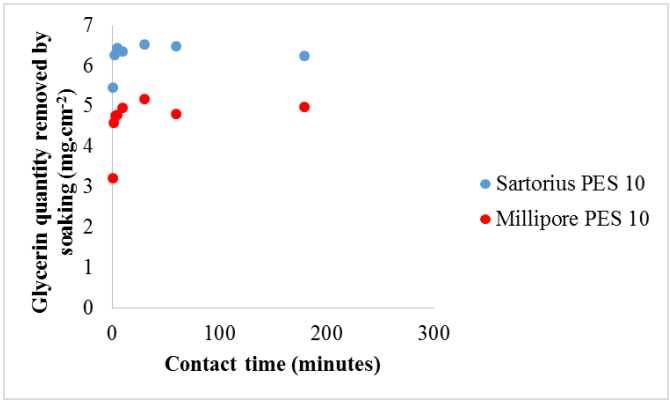

Fig. 9. Variation of total glycerin quantity removed (mg.cm^{-2}) by soaking as a function of contact time [Sartorius-Millipore, PES, 10 kDa, distilled water, S = 14.5 cm²].

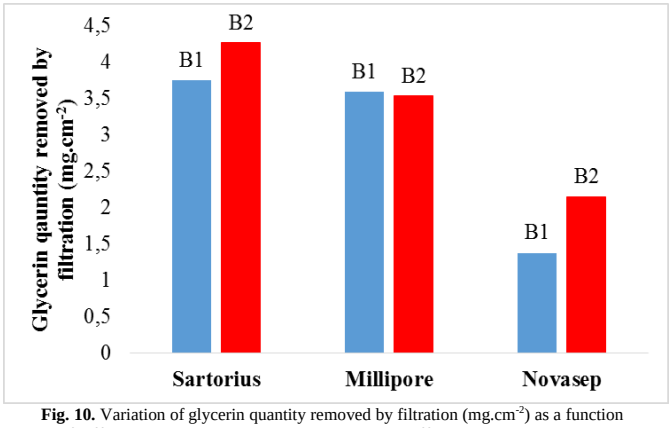

Fig. 10. Variation of glycerin quantity removed by filtration (mg.cm^{-2}) as a function of different PES 10 kDa membrane suppliers and different batches B1 and B2.

4. Conclusions

Glycerin removal protocols were studied for a wide range of ultrafiltration flat sheet membranes, supplied from different manufacturers (i.e. Millipore, Sartorius, GE Osmonics, Novasep and Pall). The used membranes were made of different polymers, including PES, RC, PVDF, polysulfone and with a wide range of MWCO values (5 to 60 kDa). The initial glycerin quantity depends on the membrane characteristics. This study presents an experimental evaluation of the glycerin quantity contained in the membrane (position and quantity). Different glycerin kinetics as a function of membrane characteristics (i.e. supplier, material, MWCO, thickness, and permeability) and different operating conditions (filtration pressure, contact time) were investigated. Accurate measurement of density is a simple and effective method to study the glycerin concentration, although here there is a detection limit of 0.1 mg.mL^{-1} (corresponding to quantity of 0.07 mg.cm^{-2}). For filtration experiments and for similar permeability, the removal kinetics are similar whatever the operating parameters and type of membranes are. However, glycerin removal is not always complete and the position of glycerin in the membrane may explain this. Indeed, a greater glycerin quantity is located in the membrane separating layer compared to the membrane support. Moreover, the glycerin quantity in the support is very difficult to remove by filtration. However, this is easily solved by soaking method.

Furthermore, the homogeneitys of glycerin distribution influences its removal, too. The results showed that the total quantity removed by filtration is lower than that by soaking, even for a short contact time. It is difficult to provide the initial glycerin quantity, because it depends on membrane

manufacturer and membrane characteristics (i.e. MWCO, material, thickness, and permeability). In conclusion, the glycerin quantity contained in the ultrafiltration flat sheet membrane is not negligible and the results indicate the difficulty to remove it, completely, by filtration method. This removal will be more important and faster with soakings in different baths.

5. References

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