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Synthesis, characterization and performance of membranes for clarification of lemon juice

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ABSTRACT

Two membranes named M1 and M2 from polysulfone (PSF) and polyvinylidenefluoride (PVDF), respectively, were prepared in our laboratory in order to determine their structural characteristics and to evaluate their efficiency in lemon juice clarification. Both membranes were characterized by scanning electron microscopy (SEM), liquid–liquid displacement, contact angle measurements, and the water permeability (L_h). Asymmetric membranes with a sponge-like and finger-like substructure for M1 and M2, respectively, were obtained. M1 PSF membrane had a smaller pore size and a higher porosity than PVDF but it had a higher value of permeate flux and lower fouling. The quality of clarified juice was evaluated in terms of: total soluble solids (TSS), suspended solids (TS), pH, citric acid content (% citric ac.). The resulting clarified lemon juice was highly similar to the initial juice but the reduction of the hesperidin (HSP) was lower for M2 (34%) when is compared to M1 (41%).

Keywords: Lemon juice; Ultrafiltration; Permeate flux; Quality control

1. Introduction

Argentina processes 45% of the world lemon production and more than 90% is industrialized in the south hemisphere. New methods are necessary to be developed in order to improve the quality of the product—with similar characteristics to fresh juices and free of chemical preservatives—and to minimize the cost of the process.

Argentina produces concentrated of citric juices with exceptional attributes of quality (color, flavor, pulp proportion and soluble solids/acidity relationship) that confer advantages in the international market. Other characteristics that differentiate them with respect to juices produced by other countries are lower isocitric acid content and higher vitamin C concentration [1,2].

The most used clarification process in the Argentinian industry consists on a first stage of enzymatic despectinized. Then the juice is processed with a flocculant and activated carbon which is added to discolor the juice. After that, the juice is filtered again. Finally, a pasteurization process is carried out to diminish the microbial load and to disable the enzymes present in the medium. The main disadvantage of this process is that the clarified juice presents different organoleptic and nutritional characteristics with respect to the untreated juice.

The main advantages in the membrane technology are the following: (1) reduction of clarification times, (2) simplification of the clarification process, (3) high selectivity, which implies the reduction of microbial

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load, (4) low energy requirements, (5) the possibility of operating at room temperature and preserving the juices freshness, aroma and nutritional value, improvement of the quality of the final product through the removal of extraneous substances and improvement of the production processes [3–5].

However, the disadvantage in this process is the membrane fouling during the permeation, that causes a quick decrease of the permeate flow [5–8].

In juice clarification process with membranes, it is useful to understand the impact of the polymer material on membrane structural characteristics and on the process performance. For this reason, in this work we have prepared two membranes from polysulfone (PSF) and polyvinylidenefluoride (PVDF) in order to determine their structural characteristics and to evaluate their efficiency in lemon juice clarification.

2. Experimental

2.1. Preparation of the membranes

Polyvinylidene fluoride (PVDF high viscosity Solef® 1015, Solvay Belgium) and polysulfone (PSf UDEL® P–3500, Amoco) were used to prepare asymmetric membranes by phase inversion process [9]. The solvent was *N*,*N*-dimethylformamide (DMF, analytic grade) of Merck. Membranes were prepared with a solution of 18 wt.% of polymer in DMF. Once extended the polymeric solution on the support (Viledon 2430, non-woven support of polyethylene/polypropylene, Carl Freudenberg, Germany), it was immersed in a bi-distillated water bath at 25 °C. Then, polysulfone (M1) and polyvinylidenefluoride (M2) membranes were stored in water.

2.2. Microscopy

The morphology of the membranes was studied using a scanning electron microscope (LEO 1450 VP). Membranes embedded in isopropanol were submerged in liquid nitrogen to fracture them and then were coated with a thin layer of gold.

2.3. Pore size measurement by liquid–liquid displacement

The procedure consists of absorbing the membrane with a liquid (the wetting liquid–isobutanol saturated in water and methanol – 15/25/7 v/v/v) and then to displace it from the pores with the aqueous phase. The flow through the membrane is carried out with gradual increments of flow on the aqueous phase side, by a syringe pump (ISCO 500D). The balanced pressure is measured simultaneously in each incremental step by a pressure transducer (OMEGA DP200).

Cantor's equation allows us to calculate the radii of pores for each applied pressure:

$$r_p = \frac{2\gamma}{\Delta p} \tag{1}$$

where Δp is the applied pressure, γ is the interfacial tension and r_p is the pore equivalent radium.

Assuming that the pores cylindrical, the Hagen–Poiseuille relationship can be used for correlating the volumetric flux density, J_{vi}, with a given pore radius, r_p. In order to obtain the pore number distributions (dn_i/dr_{pi}) the second derivative of Hagen–Poiseuille equation was calculated as a function of applied pressure:

$$\frac{dn_i}{dr_{pi}} = -\frac{\eta\tau l\Delta p_i^6}{16\pi\gamma^6}\frac{d^2J_{vi}}{d\Delta p_i^2} \tag{2}$$

where η is the dynamic viscosity; τ, the tortuosity; and l, pore longitude which corresponds to dense layer thickness [10,11].

2.4. Flow of pure water

The hydraulic permeability (L_h) is given by the following expression:

$$L_h = \frac{J_v}{\Delta p} \tag{3}$$

where J_v is the permeate flux, and Δp is the transmembrane pressure. Hydraulic permeability was performed using an ultrafiltration cell Minitan-S of Millipore Corp. The membrane was placed into permeation cell at a constant feed flow rate of 1150 ml/min. The experimental protocol was as follows: first, the membrane was compacted to a transmembrane pressure of 100 kPa for 30 min [12]. Then the range of applied pressure was from 100 to 20 kPa and the pure water flows were measured [13].

2.5. Contact angle measurements

The contact angles between membrane and three liquids were measured by using a contact anglometer 1501 of Micromeritics. To determine both the hydrophobic and hydrophilic contributions of the membrane surface in the contact angle is determined with three different liquids (water, glycerol and decane), and a system of three equations with three unknowns (γ_S^{LW}, γ_S^+ and γ_S^-) is solved, using the equation of Young–Dupre:

$$(1+\cos\theta)\gamma_L^{Tot} = -\Delta G_{SL} = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} \tag{4}$$

where θ is the contact angle value among the liquid (L) and the surface of the membrane (S) and γ_L^{Tot} is the superficial tension of the liquid. The parameters γ_L^{LW}, γ_L^+ and γ_L^- are tabulated [14]. The results are expressed as a percentage of the total interaction energy ($\%\Delta G_{SL}^{LW} > 50$ or $\%\Delta G_{SL}^{AB} < 50$ can be considered hydrophobic surfaces and $\%\Delta G_{SL}^{AB} < 50$ or $\%\Delta G_{SL}^{AB} > 50$, can be considered hydrophilic surfaces), where LW refers to the interactions of Lifshitz–van der Waals (non-polar) and AB refers to the interactions of Lewis acid-base (polar).

2.6. Clarification of lemon juice

The lemon juice was obtained from fresh fruit, by pressing and filtering with a 50-mesh-filter.

The equipment used in the clarification process was the same as hydraulic permeability, using a peristaltic pump to feed the juice in the cell. A previous compactation of the membrane with distilled water during 30 min was made. The experimental conditions were the following: feed temperature: 20 °C, feed flow: 1.15 l/min and transmembrane pressure: 60 kPa. During the permeation the retained one was totally recirculated and the clarify one was continuously collected.

2.7. Juice analyses

The acids content was titrated to pH 8.2 with 0.1 N NaOH and expressed as percent citric acid. pH was measured by a multiparametric pH meter (Waterproof Combo, Hanna). Suspended solids (TS) were determined in relation to total juice (w/w%) by centrifuging, at 3300 rpm for 15 min, 10 ml of a pre-weighted sample; the weight of settled solids was determined after removing the supernatant. TSS measurements were carried out by using an automatic GPR 11–37 refractometer (Index Instruments) and expressed in °Brix. The concentration of hesperidin (flavonoid) was determined spectrophotometrically by the method of Davis [15].

3. Results and discussion

SEM micrographs in Figs. 1 and 2 show the asymmetric structure of M1 and M2. The general structures of membranes consist of a skin layer on top and below an intermediate layer with a sponge-like and finger-like substructure for M1 and M2, respectively.

Since PSF is more hygroscopic than PVDF, when the polymeric solution is extended, PSF absorbs the atmospheric moisture in a higher grade. As a result, the rate of exchange between the solvent and nonsolvent during the phase inversion process decreases, which causes the suppression of the macrovoids. This effect is similar to that found by other authors [16] where a decrease of

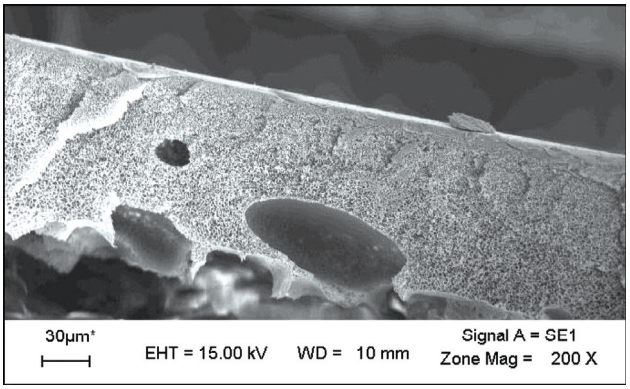

Fig. 1. Cross section of M1 200 X.

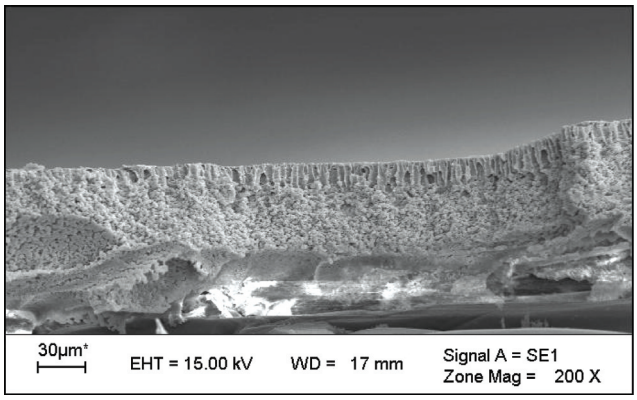

Fig. 2. Cross section of M2 200 X.

macrovoids in the porous substructure was obtained by adding water to casting solution.

The results of the membrane characterization are shown in Table 1. Both, r_p and porosity measurements are reported from liquid–liquid displacement. Contact angle between water membrane was obtained 3 min after dropping water on the surface.

The PSF membrane has the highest L_h, which can be attributed in part to its higher porosity and higher hydrophilic superficial contribution (higher $\%\Delta G_{SL}^{AB}$ %), despite having more contact angle of water-membrane surface.

The pore radius distributions for both membranes are shown in Figs. 3 and 4. It can be observed that the pore size for M1 and M2 membranes is in the suitable range for juice clarification and microbial agent retention. However, a slight diminution of pore size can be explained because PVDF casting solution has more viscosity than the PSf one. As it is commonly pointed out in literature [11], an increase in the viscosity of the casting

Table 1
Membrane structural parameters

	L_h (L/m²h bar)	Porosity (ε)	r_{pMean} (nm)	$\%\Delta G_{SL}^{LW}$	$\%\Delta G_{SL}^{AB}$
M1	72.00	0.33	30.20	46.53	53.47
M2	21.60	0.20	48.50	57.60	42.40

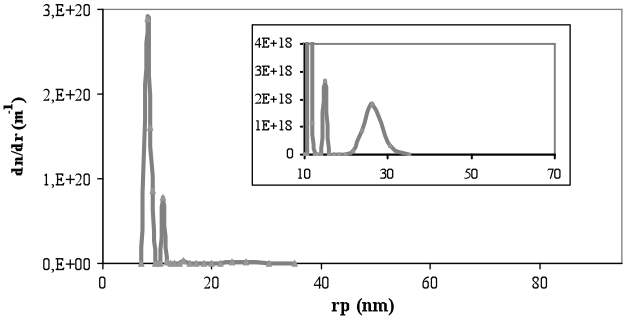

Fig. 3. Pore radii distribution for M1.

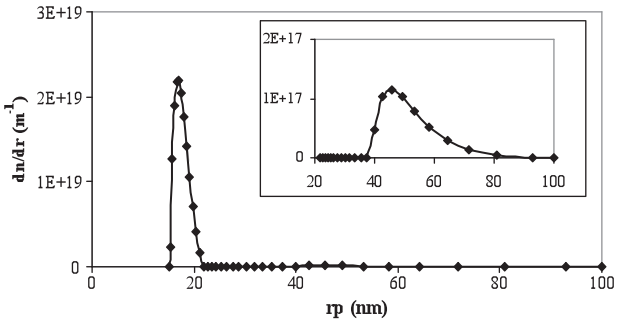

Fig. 4. Pore radii distribution for M2.

solution causes kinetic hindrance against phase separation leading to a diminution of pore size.

The preliminary assays of permeation were carried out in a Minitan-S cell. The membranes were compacted with distilled water during 30 min. Then the lemon juice clarification test was performed with the same pressure and feed flow. Fig. 5 shows the variation of the flux vs time for selected working conditions. The permeated flux falls strongly during the first 6–8 min until reaching stationary state.

This fall of flux is attributed to the large amount of suspended solids that is deposited on the membrane blocking its pores, and generating the formation of a gel

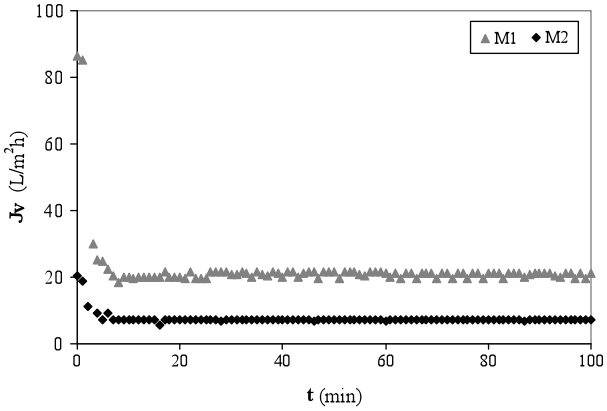

Fig. 5. Permeate flux during the filtration of the lemon juice.

layer or cake [17,18]. The permeation flux of M1 (60 min. after the juice was introduced in the feed (J_{v60})) is approximately three times greater than that obtained for M2, indicating a lower fouling, which could be due to its lower hydrophobicity as it presents a smaller pore size.

Table 2 shows the most relevant physicochemical characteristics for the original lemon juice (feed) and the clarified juice (permeate) for each membrane.

The clarificated juice by using M1 presents similar values of % citric ac., pH and TSS when is compared to untreated lemon juice, while the values obtained for the permeated juice with M2 are lower. Both clarified juices from M1 and M2, do not have permeated total solids, showing a soft yellow translucent appearance (Fig. 6). Total solids remained totally concentrated in the retentate. The value of HSP for both clarified juices is lower, than the untreated juice. Although the juices obtained from membrane technology can have different properties according to the membrane material used, they maintain attributes similar to the untreated juices. This result agrees with the informed one by other authors in another type of juices (Kiwifruit juice [2], Apple juice [19], Lemon juice [5]).

4. Conclusions

In this work, membranes from 18 wt.% of PSF and PVDF were obtained with different pore sizes and porosity for the treatment of lemon juice. PSF is a more hydrophilic polymer which was used to prepare membranes that showed a sponge-like substructure, while PVDF membranes presented a finger-like structure.

M1 (PSF) membrane had a smaller pore size and a higher porosity than PVDF but it had a higher value of permeate flux and less fouling. However, a lower value of HSP due to his smaller pore size was found in the permeated juice.

Table 2
Values obtained in the quality control techniques

	% Citric ac.	pH	%TS	TSS (°Brix)	C_{HSP} (×10⁴ M)	J_{v60} (L/m² h)
M1 Feed	6.98	1.86	0.54	8.14	2.17	
Perm. (percent)	6.21 (88.96%)	1.90	0 (0%)	7.14 (87.71%)	1.29 (59.42%)	20.59
M2 Feed	6.29	2.54	0.52	7.32	2.52	
Perm. (percent)	3.67 (58.34%)	2.60	0 (0%)	4.71 (64.34%)	1.65 (65.62%)	7.11

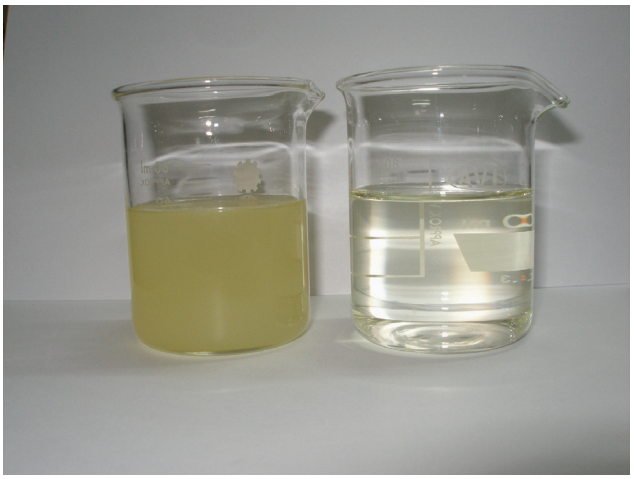

Fig. 6. Feed and permeate obtained with M1.

The results show that the clarification of juices with polymeric membranes is an interesting option to be considered in industry. This is due to that the membranes allow obtaining high quality juices, maintaining the physical–chemical characteristics of the juices, and the most important advantage is that the clarification process works at low temperature. Indeed, this process does not need an additional step of pasteurization, preserving the flavor and aroma of fresh juice, according to current market requirements.

Symbols

Δp	—	Transmembrane pressure, Pa
r_p	—	Pore equivalent radium, m
J_{vi}	—	Volumetric flux density, l/m² h
n_i	—	Pore number
dn_i/dr_{pi}	—	Pore number distribution, m⁻¹
l	—	Pore longitude, m
L_h	—	Hydraulic permeability, l/m² h bar
ΔG_{SL}	—	Free energy of interaction, J
ΔG_{SL}^{LW}	—	Free energy of hydrophobic interaction (Lifshitz–van der Waals interactions), J
ΔG_{SL}^{AB}	—	free energy of hydrophilic interaction (Lewis acid–base interactions), J

Greeks

γ	—	Interfacial tension, N/m
η	—	Dynamic viscosity, Pa s
τ	—	Tortuosity
Θ	—	Contact angle (°)
γ_L^{Tot}	—	Superficial tension of the liquid, N/m
γ_L^{LW}, γ_L^+ and γ_L^-	—	Surface tension parameters, N/m
γ_S^{LW}, γ_S^+ and γ_S^-	—	Surface energy parameters, N/m

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