Contents lists available at SciVerse ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Impact of structural and textural membrane properties on lemon juice clarification

P.M. Chornomaz[a], C. Pagliero[b], J. Marchese[a], N.A. Ochoa[a,*]

[a] Instituto de Física Aplicada – INFAP, Universidad Nacional de San Luis, CONICET-FONCYT, Argentina
[b] Facultad de Ingeniería, Universidad Nacional de Rio Cuarto, CONICET-FONCYT, Chacabuco, 917-5700 San Luis, Argentina

ABSTRACT

Lemon juice was clarified using membranes with different structural and textural properties. Membranes were prepared from 0, 5, 7 and 10 wt.% of PVP in PVDF and they were structurally and functionally characterized. Results indicated that the addition of PVP produced both structural and surface textural changes in the membranes. These textural changes resulted in an increase of apparent hydrophobicity in the membranes prepared from 5 and 7% of PVP in the casting solution. Besides, the presence of residual PVP in the membrane favors hesperidin adsorption enhancing its retention. Analysis of the clarified juice indicated that the membrane prepared with 5% of PVP possessed the highest efficiency, combining high permeate flux and high juice quality.

Keywords: Lemon juice; Clarification; Ultrafiltration; Roughness; Membrane

Nomenclature

A	effective membrane area (m^2)
J_v	volumetric flux ($L\,m^{-2}\,h^{-1}$)
L_h	hydraulic permeability ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
R	Wenzel roughness factor
r_{pm}	mean pore radium (m)
Δp	transmembrane pressure (Pa)
ε	porosity
θ	contact angle (°)

1. Introduction

Results of epidemiologic studies (Kaur and Kapoor, 2001) suggest that a high consumption of fruit reduces the risk of suffering cardiovascular disease, cancer and neurological disorders. Lemon (*Citrus lemon*) is a rich source of important chemical compounds, including citric acid, ascorbic acid, minerals and flavonoids. Although their health related properties have always been associated with their high vitamin C content, it has recently been proved that flavonoids have several biological functions, including anti-inflammatory, anti-allergic, anti-viral, antiproliferative, anti-mutagenic, anti-carcinogenic and anti-oxidant activities. The latter is due to a neutralization of free radicals, responsible of aging and oxidative stress in cells (Middleton and Kandaswami, 1992; Manthey and Grohmann, 1996; Manthey, 2004; Benavente-García et al., 1997; Benavente-García and Castillo, 2008; Del Río et al., 2004; Tripoli et al., 2007).

The most abundant flavonoids in lemon are hesperidin, eriotricin and diosmin. Hesperidin, its main flavanone, has venotonic and vasoprotective properties (they reduce capilar permeability and enhance its resistance). It also has analgesic, antioxidant and antiinflammatory properties (Galati et al., 1994; Monforte et al., 1995; Leuzzi et al., 2000; Vanaclocha and Cañigueral, 2003; Del Río et al., 2004; González-Molina et al., 2009).

Nowadays there is an increasing demand for obtaining citric juices with features typical of natural, additive free juices, due to the fact that during industrial transformation, thermal damage and chemical oxidation degrade the most sensitive components of juices, reducing the quality of the final product. This implies the research of new technologies capable of improving the nutritional, sensory and microbiological quality of citric juices.

* *Corresponding author*. Tel.: +54 2652 446211.
E-mail address: aochoa@unsl.edu.ar (N.A. Ochoa).
Received 20 December 2010; Received in revised form 29 November 2012; Accepted 3 December 2012
0960-3085/$ – see front matter © 2012 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fbp.2012.12.001

The use of membrane processes, such as microfiltration (MF) and ultra-filtration (UF) in the clarification of citric juices has lately gained importance over some conventional treatments including diatomaceous earth, paper filters, bentonite, etc. (Jiao et al., 2004; Cassano et al., 2007). This is due to the fact that membrane processes have the advantage that separation occurs at room temperature (without loss of aromatic volatile substances), high selectivity – implying the reduction of microbial load, no need of additives to boost separation and very low electricity consumption. However, the major disadvantage of this process is membrane fouling during permeation caused by the retention of some components over the surface of the membrane, causing a rapid decrease of flux (Mondor et al., 2000; De Bruijn et al., 2002; Carneiro et al., 2002; Cassano et al., 2003; Espamer et al., 2006). Flux and product quality are two important aspects to consider when selecting the membrane clarification process. High flux is essential for a practical and economic filtration. The quality of the product must reach the level of at least other standard methods. The flux through the membrane and its selectivity are defined by the physical structure of the membranes and the kind of physicochemical interaction between them and the lemon juice. Therefore, the aim of this work was to prepare polymeric membranes with the addition of different concentrations of polyvinylpyrrolidone (PVP) used as an additive. The addition of PVP to the casting solution causes changes in the structural and textural properties of membranes. These changes are analyzed and related to the efficiency of the lemon juice clarification process.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) (High viscosity PVDF Solef® 1015) provided by Solvay Belgium was used as membrane material. The solvent used was N,N-dimethylformamide (DMF, analytical grade, Merck).

Polyvinylpyrrolidone (PVP K30 Mw = 40,000 Da) provided by Fluka was used as an additive in the PVDF/DMF solution. A polypropylene non-woven fabric (FO2430), 0.45 μm thick, kindly provided by Carl Freudenberg, Germany, was used as support.

NaOH, methanol and isobutanol were supplied by Merck; diethylene glycol and phenolphthalein by Sigma–Aldrich. Lemon juice was obtained by squeezing fresh fruit and filtering it with a 50-mesh sieve.

2.2. Membrane preparation

Membranes were prepared by phase inversion process (Kesting, 1985). The FO 2430 support was adhered to a 20 cm × 30 cm glass plate. The polymeric solution was cast on the support using a chromatographic extensor at 375 μm wet thickness. Then, the casting solution (nascent membrane) was immersed in a bi-distilled water bath (4.5 L) 25 °C. The membrane was stored in water bath until use. Details of the casting solution composition for PVDF–PVP membrane preparation are given in Table 1. Membrane preparation was carried out in triplicate.

Table 1 – Composition, in DMF, of casting solution used to prepare the membranes.

Membrane	PVDF (wt.%)	PVP (wt.%)
M1	18	–
M2	18	5
M3	18	7
M4	18	10

2.3. Membrane characterization

2.3.1. Scanning electron microscopy (SEM)

Membrane morphology was analyzed using a scanning electron microscope (LEO 1450VP, Leo Electron Microscopy Ltd.). The membranes samples to be examined by SEM were cut out, soaked in isopropanol and freeze-fractured in liquid nitrogen. Membrane samples were sputtered with gold and the SEM photographs of cross-sections were taken.

2.3.2. Pore size measurement by liquid–liquid displacement porosimetry (LLDP)

Three liquids (mixture of isobutanol/methanol/water; 15/7/25, v/v/v) (surface tension, $\gamma = 0.35$ mN/m) were used to analyze pores applying relatively low pressures (Calvo et al., 2004). The procedure consists in soaking the membrane with a liquid (the wetting liquid, aqueous phase) and then displacing it from the pores with the organic phase, (isobutanol saturated with water and methanol). Flux through the membrane is obtained by using a syringe pump (ISCO 500D) to gradually increment the flux on the organic-phase side. Simultaneously, equilibrium pressure is measured in each incremental stage using a pressure transducer (OMEGA DP200). A more detailed description of the method is reported in elsewhere (Masuelli et al., 2012). Once the pore size distribution for each membrane was determined, the mean pore radius of distribution was reported as r_{pm}. All experimental trials were repeated in three different membrane samples.

2.3.3. Hydraulic permeability

Determination of hydraulic permeability was carried out using an ultrafiltration device shown in Fig. 1. The Minitan-S by Millipore Corp permeation cell is made of acrylic material with nine rectangular ducts with a width 0.4×10^{-3} m, a height 7×10^{-3} m and a length of 5.5×10^{-2} m each and the

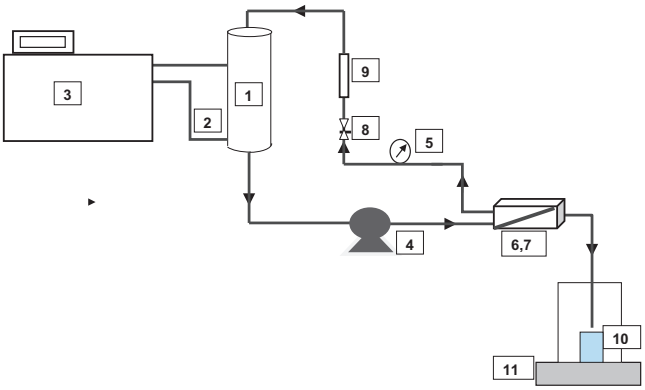

Fig. 1 – Permeability equipment: 1 – Liquid under study. 2 – Thermostabilized reservoir. 3 – Thermostatic bath. 4 – Peristaltic pump. 5 – Pressure gauge. 6 – Permeation cell Minitan-S. 7 – Membrane. 8 – Needle valve. 9 – Flowmeter. 10 – Sampling glass. 11 – Analytical balance.

transversal section of the channel is 2.8×10^{-6} m^2. The effective transfer area is 3×10^{-3} m^2.

The membrane was placed in the permeation cell and the pure water was pumped through the membrane surface at a constant feed flow of 1.15 L/min. The experimental protocol was as follows: first the membrane was compacted at a transmembrane pressure of 1 bar for 30 min (Persson et al., 1995). Then, the hydraulic permeability was determined from measurements of pure-water fluxes at different pressures (0.2–1 bar) (Ochoa et al., 2006). Hydraulic permeability coefficient (L_h) was calculated with the following expression:

$$L_h = \frac{J_v}{\Delta p} \quad (4)$$

where J_v is the permeate flux (L m^{-2} h^{-1}), and Δp is the transmembrane pressure (bar). All permeation trials were carried out in triplicate.

2.3.4. Contact angle measurement

The relative hydrophobicity of a membrane can be observed in the analysis of the contact angle (θ) between a membrane and a fluid in such a way that solid–liquid interface is characterized by the value of θ. The higher the value of θ, more hydrophobic the surface is.

The contact angle between water and membrane was measured using the sessile drop method, determining the angle of contact from the profile tangent of the drop after photographing it with a digital camera – Olympus SP-350. Using a 0.5 mL syringe a water drop was placed on the membrane surface. The values of the contact angle were measured in 5 different positions over the each dry membrane and then averaged.

2.3.5. Analysis of FT-IR

To determine the quasi-quantitatively PVP and PVDF concentration in the prepared membranes FT-IR analyses of the samples were realized. FT-IR analyses were carried out by a Varian 640-IR Spectrometer in the wavenumber range 400–4000 cm^{-1} using the ATR mode.

2.4. Clarification process

For the experiences of lemon juice clarification, the same permeation device shown in Fig. 1 was used. First membrane compaction was made with de-ionized water under $\Delta p = 0.6$ bar for 30 min. Then, the juice was circulated through the membrane unit using a peristaltic pump. Experimental conditions were the following: feed temperature T = 20 °C, feed flow Q = 1.15 L/min and transmembrane pressure $\Delta p = 0.6$ bar. During permeation the retentate was fully recycled and the clarified solution was continuously collected. Permeate flux (J_v) was determined from the mass collected. All experiments were performed with three different samples of each membrane.

2.5. Analysis of lemon juice quality

2.5.1. Determination of suspended solids

For the determination of suspended solids 10 mL of sample solution (feed or permeate) were weighed in a test tube, it was centrifuged at 3300 rpm for 15 min. The supernatant was drained placing the test tube face down for 10 min. Once dried the precipitate was weighed again in order to obtain the value of suspended solids.

2.5.2. Total acidity determination (pH)

For pH determination a pHmeter (Waterproof Combo, Hanna) was used.

2.5.3. Determination of citric acid and trititable acidity (TA)

5 mL of sample material was poured in a 50 mL flask and a given volume (45 mL) of distilled water was added. A sample of 10 mL of the solution was taken and transferred to an Erlenmeyer containing 70 mL of distilled water with 0.3 mL of phenolphtalein. The trititable acidity was determined using 0.1 N NaOH.

2.5.4. Determination of total soluble solids

The total soluble solids (TSS) were directly determined in °Brix using a GPR 11–37 automatic refractometer (Index Instruments).

2.5.5. Hesperidin (HSP) determination

Hesperidin concentration was determined with a spectrophotometer (U-2001, Hitachi) using the Davis method (Davis, 1947; Ting and Roseff, 1986). This method consists of placing 10 mL of diethylene glycol (90%) in a 25 mL flask and then adding 1.2 mL of sample material and 1.2 mL of NaOH 4 N. Then, the components were mixed and settled for approximately 10 min. After that, the absorbance was measured at 360 nm.

2.5.5.1. HSP static adsorption (primary adsorption). Due to the importance of HSP as a high nutraceutical component in lemon juice, the interaction between membranes and this compound was analyzed. Samples of the prepared membranes (area of 5 cm^2) were contacted with lemon juice (10 mL). The remaining HSP in the solution was determined according with the Davis method. All adsorption assays were replicated three times.

3. Results and discussion

3.1. Membrane characteristics

Fig. 2 shows cross sections of the membranes fractured in liquid N_2. An increase in membrane thickness with PVP contents similar to that reported by Curcio et al. (2006) can be observed. General structures were very similar, consisting of a skin layer on top and below an intermediate layer with a finger-like structure.

The PVP content in the casting solution was chosen as the independent variable to study the determination of the statistical significance of the obtained results. Mean pore, porosity, contact angle and hydraulic permeability (L_h) of membranes were chosen as dependent variables (or evaluated responses). Data were analyzed using software Statgraphics plus version 5.1. The significance of each model was tested by Analysis of Variance (ANOVA). Significant differences (P-values < 0.05) were found between structural membrane parameters for different PVP ratios.

Table 2 summarizes the main structural properties of the skin layer, r_{pm} and ε, from LLDP measurements of the different PVDF-PVP prepared membranes. The membrane hydraulic permeabilities were also included. These results show that a minimum pore radius ($r_{pm} = 15 \pm 1$ nm) is obtained for 5% PVP membrane with a relatively high L_h (250 ± 16 L m^{-2} h^{-1} bar^{-1}). This high L_h can in part be attributed to the high membrane surface porosity ($\varepsilon = 0.34 \pm 0.07$). The membrane with 10% PVP

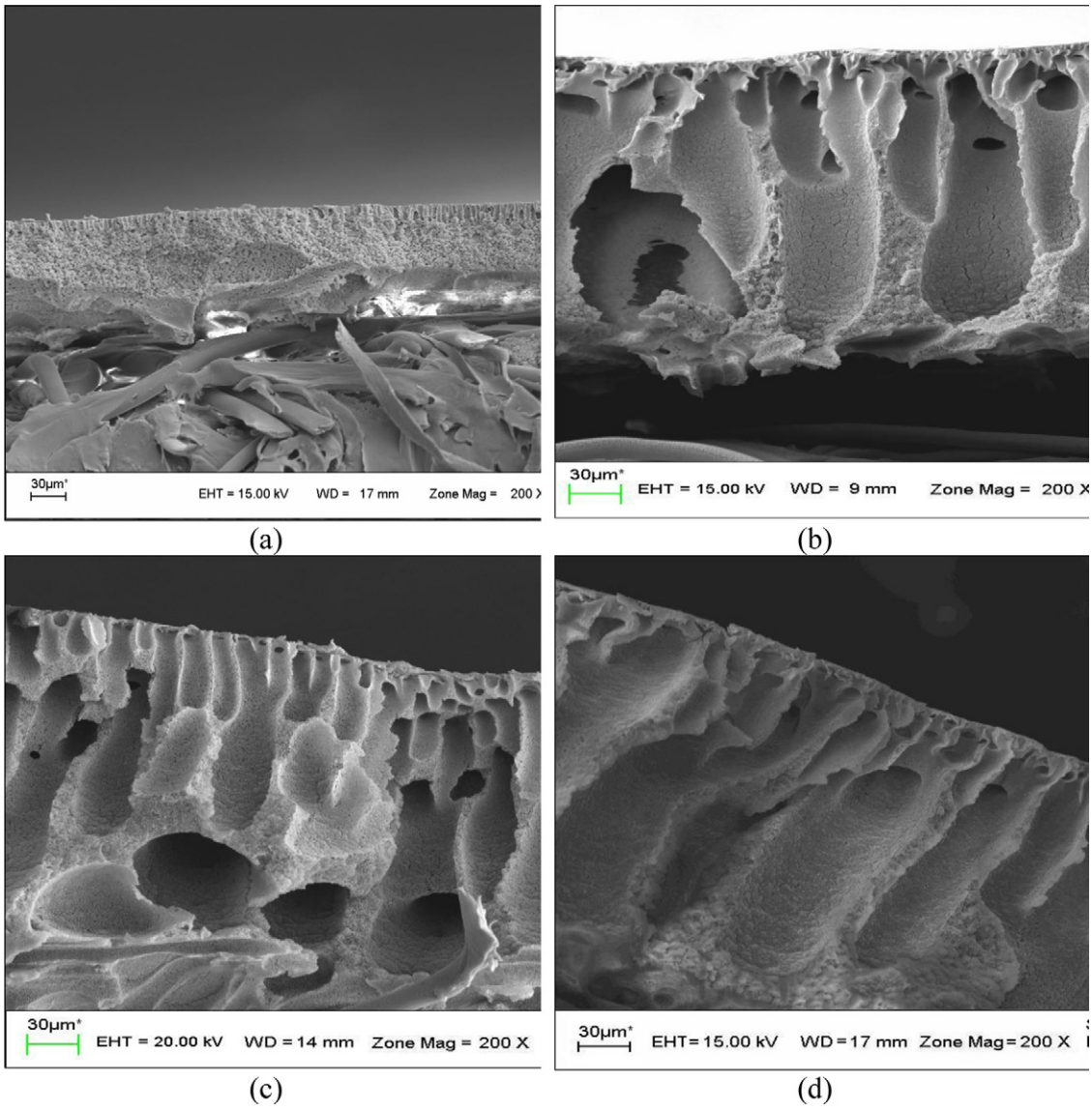

Fig. 2 – SEM micrographs of the transversal section of: (a) M1; (b) M2; (c) M3; and (d) M4.

had the highest value in L_h ($360 \pm 50\,L\,m^{-2}\,h^{-1}\,bar^{-1}$) as a consequence of its high mean pore radius ($r_{pm} = 420 \pm 70$ nm). Thermodynamic and rheological data obtained in several studies (Tam et al., 1993; Han and Nam, 2002; Tarboush et al., 2008) suggest that phase separation in the casting solution is influenced by the complex correlation between thermodynamic enhancement and rheological hindrance that can be attributed to PVP addition. As a nonsolvent additive, PVP produces two opposite effects. It reduces the miscibility of the casting solution with water (used as nonsolvent during the phase inversion), which causes thermodynamic enhancement of the phase separation. At the same time, it increases the viscosity of the solution (rheological factor), which causes kinetic hindrance against phase separation. Depending on the PVP content, thermodynamic or rheological factors will have a more important impact on the morphology and performance of the membrane (Wang et al., 1999). In 15 wt.% polysulfone (PSf) membrane series reported by others authors (Tam et al., 1993; Han and Nam, 2002) flux increases about nine times as 5% PVP is added in casting solution. Beyond 5%, more PVP in the casting solution produces less flux (Lafrenière et al., 1987). Several authors have studied the effect of PVP on L_h and they have found a maximum value at different PVP polymer ratios (Lafrenière et al., 1987; Jacobs et al., 1992; Torrestiana-Sanchez et al., 2007). It is considered that differences in ratios with maximum L_h value are due to variations in other processing variables, e.g., solvent evaporation time and gelation temperature.

In Table 2 the apparent contact angle values (θ^*) determined in this study are also shown. PVDF is a polymer with very

Table 2 – Structural, textural and functional properties of membranes.

Membrane	r_{pm} (nm)	ε	θ^*	R	L_h ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
M1	48 ± 4	0.20 ± 0.02	52 ± 2	11.76 ± 4	22 ± 2
M2	15 ± 1	0.34 ± 0.07	64 ± 2	1.69 ± 0.1	250 ± 16
M3	290 ± 42	$0.001 \pm 1.1 \times 10^{-4}$	65 ± 3	1.23 ± 0.2	180 ± 14
M4	420 ± 70	$0.002 \pm 1.3 \times 10^{-4}$	59 ± 1	1.09 ± 0.05	360 ± 50

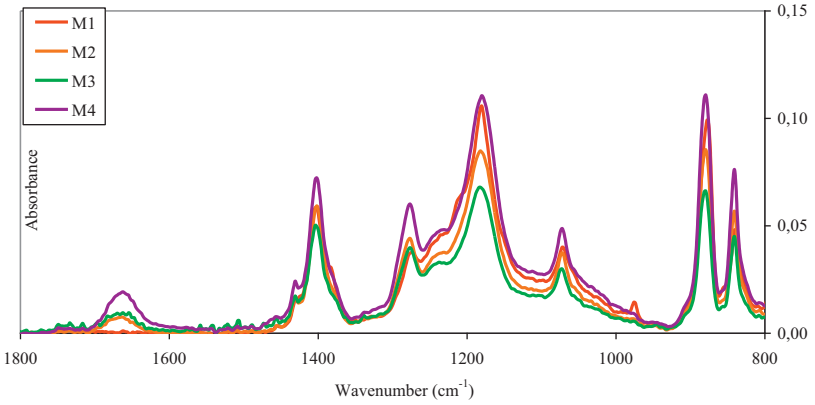

Fig. 3 – FT-IR spectrums of prepared membranes.

little hydrophilicity; its contact angle has been reported to be between 80° and 90° by other authors (Liu et al., 2011; Gryta and Barancewicz, 2010). Discrepancies with the values reported in this paper can be attributed to the effect that surface texture has on the values of the contact angle. Wenzel's relation (Wenzel, 1949) establishes that the cosine of the apparent contact angle increases linearly with the cosine of the angle of a flat surface (θ) of the same chemical composition, which can be represented in the following equation:

$$\cos\theta^* = R\cos\theta \quad (9)$$

where R is the surface roughness factor (or Wenzel roughness factor). The former indicates that rough surfaces improve moistening in the case of hydrophilic surfaces ($\theta < \pi/2$). To observe this behavior a non-porous PVDF thick film from a solution of 5% in DMF, evaporating the solvent at 60 °C, was prepared and its contact angle measured. The obtained value of contact angle was $\theta = 87° \pm 3°$.

Generally the PVP amount present in the PVDF–PVP cast membrane was different than the original casting solution. It is well known that PVP is dissolved and dragged in part by the nonsolvent (water) in the process of phase inversion and it remains entangled in part within PVDF. Thus, the concentration of PVP remaining in membranes M2, M3 and M4 can be established quasi-quantitatively by measuring the relationship of intensities between a characteristic PVP band and a characteristic PVDF band by FTIR. For that purpose, the 1660 cm^{-1} PVP band and the 1405 cm^{-1} PVDF band (see Fig. 3) were selected. The band intensity relations allowed the establishment of a concentration of 2.22% of PVP remaining in the M2, 3.26% for M3 and 4.65% for M4. Therefore, dense films were prepared with these concentrations and their contact angles were measured finding $\theta = 74 \pm 3°$ for M2, $\theta = 71 \pm 3°$ for M3 and $\theta = 62 \pm 2°$ for M4. Considering Wenzel's equation it can be observed that these membranes have a texture, where the measured contact angle is smaller than the contact angle of a flat surface with the same chemical composition. The roughness factor values indicated in Table 2 show that the membrane surface texture also varies with the addition of PVP. A decrease of R occurs when the PVP concentration increases, a behavior that is similar to that informed in a previous study (Ochoa et al., 2001). Also, it is important to highlight that M2 and M3 have the least hydrophilic character of the series due to their surface texture and chemical composition.

3.2. *Lemon juice clarification assays*

From the results obtained in clarification assays (Fig. 4) it can be observed that when lemon juice is incorporated in the feed stream, a marked continuous decline in permeate fluxes was observed within the first 6–8 min. Afterwards, the permeate fluxes started to be stabilized reaching the pseudo steady state (J^*). This behavior could be attributed to several simultaneous coexisting phenomena involved during the permeate flux decay such as: solute adsorption onto the membrane surface, pore blocking, concentration polarization and cake layer formation. When the PVP addition was analyzed, an increase in the pseudo steady state flux (J^* measured at $t = 60$ min) is observed. The J^* values were 7 ± 0.4; 23 ± 3; 22 ± 3 and 27 ± 3 L m^{-2} h^{-1} for M1, M2, M3 and M4, respectively. The membrane without PVP (M1) presented the lowest flux value.

Table 3 shows the quality parameters values obtained from the analytical determinations performed in feed and permeate during lemon juice clarification. Percentage values in permeates are compared to the values determined in the feed. The suspended solids were completely removed from the juice for all the membranes tested. In all cases a totally clarified juice was obtained.

It is desirable that the clarified juice has the same relation of nutraceuticals and sugar as the original feed juice, i.e. the relation $(C_{HSP}/TSS)_P$ in the permeate should be as similar

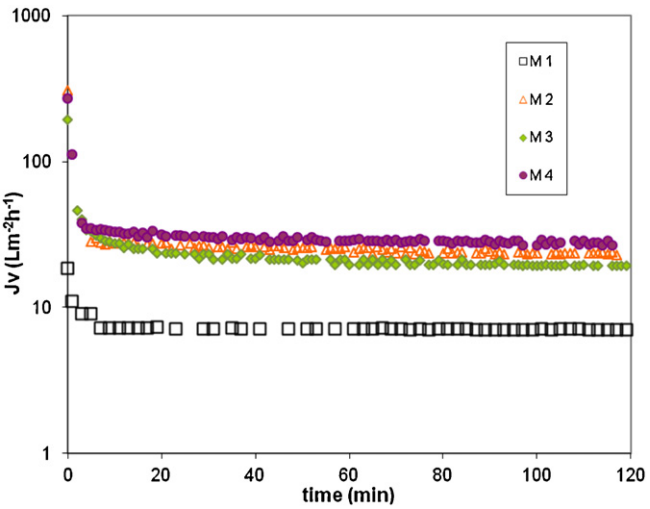

Fig. 4 – Juice permeate decay curves.

Table 3 – Quality parameters of lemon juice.

Membrane	TA	% citric acid	pH	TSS (°Brix)	C_{HSP} ($\times 10^4$ M)	$(C_{HSP}/TSS)_P/(C_{HSP}/TSS)_F$	J^* (L m^{-2} h^{-1})
Feed	981 ± 7	6.25 ± 0.3	2.54 ± 0.2	8.20 ± 0.6	2.52 ± 0.07		
M1 perm.	570 ± 6	3.56 ± 0.2 (57%)	2.6 ± 0.01	5.16 ± 0.4 (62.92%)	1.66 ± 0.3 (66%)	1.04 ± 0.17	7 ± 0.4
M2 perm.	884 ± 11	5.62 ± 0.5 (90%)	2.58 ± 0.02	7.62 ± 0.6 (93%)	2.11 ± 0.2 (84%)	0.86 ± 0.12	23 ± 3
M3 perm.	878 ± 10	5.58 ± 0.4 (89.23%)	2.55 ± 0.02	7.72 ± 0.4 (94.14%)	0.4 ± 0.03 (15.8%)	0.16 ± 0.07	22 ± 3
M4 perm.	910 ± 13	5.75 ± 0.6 (92%)	2.52 ± 0.03	7.88 ± 0.9 (96.10%)	0.07 ± 0.01 (2.77%)	0.03 ± 0.0012	27 ± 3

as possible to $(C_{HSP}/TSS)_F$ in the feed. Table 3 shows that M1 and M2 possessed the similar nutraceuticals/sugar ratio as the feed juice; while clarified permeate juices obtained using membranes with 7% and 10% PVP were reduced in quality. M3 and M4 retain HSP even though having bigger pore sizes. To analyze this behavior, HSP static adsorption on different prepared membranes was measured. The data obtained are shown in Fig. 5. M1 and M2 presented the lowest solute–membrane interactions. An increase in PVP content favored the adsorption of HSP, hindering the transmission of the flavonoid to the permeate side. Previous studies (Borneman et al., 2001; Zhao et al., 2008) indicated that PVP interaction with different polyphenols is mediated by hydrogen bonds. This type of solute membrane interactions seems to be present in these experiences, so by increasing the PVP content, HSP decreases in the permeate. A HPS mass balance up to 120 min of operational time in UF conditions was performed and the results were compared with static adsorption. For M4 (more adsorptive membrane) the HSP adsorbed mass (3.7 mg) was five times higher than the HPS permeated mass (0.7 mg). To summarize, PVP not only affects the structural and textural properties of membranes, but also generates interactions which influence the transmission of flavonoids toward the permeate side.

Evans and Bird (2006) reported that a moderate hydrophobic character in the prepared membranes present definite advantages over more hydrophilic materials for the processing of tea solutions. This also seems to be the case in this study where a lemon juice with high permeate flux and the same characteristics as natural juice was obtained using a membrane with a small pore size (M2) and a moderate hydrophobic character-influenced by its texture. Thus, the adsorption of hydrophilic species present in the lemon juice was avoided.

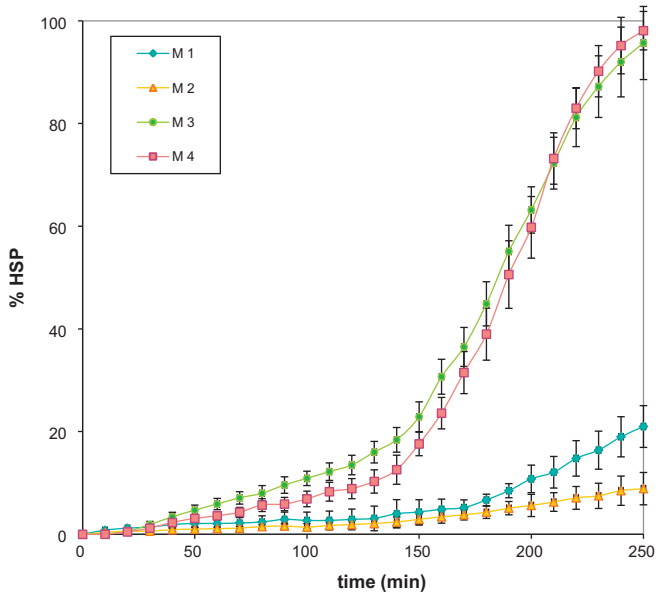

Fig. 5 – Static adsorption of HSP is expressed as percentage of HPS adsorbed respect to initial juice HSP concentration. Error bars represent standard deviation.

4. Conclusions

Lemon juice clarification was studied using PVDF based membranes with different PVP ratios. Results indicated that PVP produced changes in the membrane structures as well as textural changes in their surfaces. These textural changes resulted in membranes prepared from 5 and 7% PVP in the casting solution (M2 and M3 respectively) being relatively more hydrophilic. Besides, the presence of residual PVP in the membrane generated interactions that favored HSP adsorption hindering its transmission to the permeate side. Analysis of quality parameters of the clarified juices indicated the membrane prepared with 5% of PVP (M2) showed the highest efficiency for lemon juice clarification with high both clarified lemon juice quality and permeate flux. Membranes with relatively low hydrophilicity allow clarified lemon juice to be obtained with the same quality of natural juice.

References

Benavente-García, O., Castillo, J., 2008. Update on uses and properties of citrus flavonoids: new findings in anticancer, cardiovascular, and anti-inflammatory activity. J. Agric. Food Chem. 56, 6185–6205.

Benavente-García, O., Castillo, J., Marín, J.R., Ortuño, A., Del Río, J.A., 1997. Uses and properties of citrus flavonoids. J. Agric. Food Chem. 45, 4505–4515.

Borneman, Z., Gokmen, V., Nijhuis, H.H., 2001. Selective removal of polyphenols and brown colour in apple juices using PES:PVP membranes in a single ultrafiltration process. Sep. Purif. Technol. 22, 53–61.

Calvo, J.I., Bottino, A., Capannelli, G., Hernández, A., 2004. Comparison of liquid–liquid displacement porosimetry and scanning microscopy image analysis to characterize ultrafiltration track-etche membranes. J. Membr. Sci. 239, 189–197.

Carneiro, L., Gomez, F.S., Matta, V.M., Cabral, L.M.C., 2002. Cold sterilization and clarification of pineapple juice by tangential microfiltration. Desalination 148, 93–98.

Cassano, A., Drioli, E., Galaverna, G., Marchelli, R., DiSilvestro, G., Cagnasso, P., 2003. Clarification and concentration of food and carrot juices by integrated membrane processes. J. Food Eng. 57, 153–163.

Cassano, A., Donato, L., Drioli, E., 2007. Ultrafiltration of kiwifruit juice: operating parameters, juice quality and membrane fouling. J. Food Eng. 79, 613–621.

Curcio, E., Fontananova, E., Di Profio, G., Drioli, E., 2006. Influence of the structural properties of poly(vinylidene fluoride) membranes on the heterogeneous nucleation rate of protein crystals. J. Phys. Chem. B 110, 12438–12445.

Davis, W.B., 1947. Determination of flavanones in citrus fruits. Ind. Eng. Chem. 19, 476–478.

De Bruijn, J., Venegas, A., Borquez, R., 2002. Influence of crossflow ultrafiltration on membrane fouling and apple juice quality. Desalination 148, 131–136.

Del Río, J.A., Fuster, M.D., Gómez, P., Porras, I., García-Lidón, A., Ortuño, A., 2004. Citrus lemon: a source of flavonoids of pharmaceutical interest. Food Chem. 84, 457–461.

Espamer, L., Pagliero, C., Ochoa, N.A., Marchese, J., 2006. Clarification of lemon juice using membrane process. Desalination 200, 565–567.

Evans, P.J., Bird, M.R., 2006. Solute-membrane fouling interactions during the ultrafiltration of black tea liquor. Food Bioprod. Process. 84, 292–301.

Galati, E.M., Monforte, M.T., Kirjavainen, S., Forestieri, A., Trovato, A., Tripodo, M.M., 1994. Biological effects of hesperidin a citrus flavonoid (Note I): antiinflammatory and analgesic activity. Farmaco 40, 709–712.

González-Molina, E., Moreno, D.A., García-Viguera, C., 2009. A new drink rich in healthy bioactives combining lemon and pomegranate juices. Food Chem. 115, 1364–1372.

Gryta, M., Barancewicz, M., 2010. Influence of morphology of PVDF capillary membranes on the performance of direct contact membrane distillation. J. Membr. Sci. 358, 158–167.

Han, M.J., Nam, S.T., 2002. Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane. J. Membr. Sci. 202, 55–61.

Jacobs, E.P., Strohwald, N.K.H., Koen, D., Sanderson, R.D., 1992. Design and application of a low-molecular-mass cut-off poly(ether sulfone) membrane. Water Sci. Technol. 25, 351–362.

Jiao, B., Cassano, A., Drioli, E., 2004. Recent advances on membrane processes for the concentration of fruit juices: a review. J. Food Eng. 63, 303–324.

Kaur, C., Kapoor, H.C., 2001. Antioxidants in fruits and vegetables – the millennium's health. Int. J. Food Sci. Technol. 36, 703–725.

Kesting, R., 1985. Synthetic Polymeric Membranes, 2nd ed. John Wiley, New York, USA.

Lafrenière, L.Y., Talbot, D.F., Matsuura, T., Sourirajan, S., 1987. Effect of polyvinylpyrrolidone additive on the performance of polyethersulfone ultrafiltration membranes. Ind. Eng. Chem. Res. 26, 2385–2389.

Leuzzi, U., Caristi, C., Panzera, V., Licandro, G., 2000. Flavonoids in pigmented orange juice and second-pressure extracts. J. Agric. Food Chem. 48, 5501–5506.

Liu, F., Abed, M.R.M., Li, K., 2011. Preparation and characterization of poly(vinylidene fluoride) (PVDF) based ultrafiltration membranes using nano γ-Al_2O_3. J. Membr. Sci. 366, 97–103.

Manthey, J.A., 2004. Fractionation of orange peel phenols in ultrafiltered molasses and mass balance studies of their antioxidant levels. J. Agric. Food Chem. 52, 7586–7592.

Manthey, J.A., Grohmann, K., 1996. Concentrations of hesperidin and other orange peel flavonoids in citrus processing byproducts. J. Agric. Food Chem. 44, 811–814.

Masuelli, M.A., Grasselli, M., Marchese, J., Ochoa, N.A., 2012. Preparation, structural and functional characterization of modified porous PVDF membranes by γ-irradiation. J. Membr. Sci. 389, 91–98.

Middleton, E.J., Kandaswami, C., 1992. Effects of flavonoids on immune and inflammatory cell functions. Biochem. Pharmacol. 43, 1167–1179.

Mondor, M., Girard, B., Moresoli, C., 2000. Modeling flux behavior for membrane filtration of apple juice. Food Res. Int. 33, 539–548.

Monforte, M.T., Trovato, A., Kirjarainen, S., Forestieri, A.M., Galati, E.M., LoCurto, R.B., 1995. Biological effects of hesperidin a citrus flavonoid (Note II): hypolipidemic activity on experimental hypercholesterolemia in rat. Farmaco 9, 595–599.

Ochoa, N.A., Prádanos, P., Palacio, L., Pagliero, C., Marchese, J., Hernández, A., 2001. Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: characterisation of polyethersulfone UF membranes with dopes containing different PVP. J. Membr. Sci. 187, 227–237.

Ochoa, N.A., Masuelli, M., Marchese, J., 2006. Development of charged ion exchange resin-polymer ultrafiltration membranes to reduce organic fouling. J. Membr. Sci. 278, 457–463.

Persson, K.M., Gekas, V., Tragardh, G., 1995. Study of membrane compaction and its influence on ultrafiltration water permeability. J. Membr. Sci. 100, 155–162.

Tam, C.M., Tweddle, T.A., Kutowy, O., Hazlett, J.D., 1993. Polysulfone membranes: II. Performance comparison of polysulfone-poly-(N-vinyl-pyrrolidone) membranes. Desalination 89, 275–287.

Tarboush, B.J.A., Rana, D., Matsuura, T., Arafat, H.A., Narbaitz, R.M., 2008. Preparation of thin-film-composite polyamide membranes for desalination using novel hydrophilic surface modifying macromolecules. J. Membr. Sci. 325, 166–175.

Ting, S.V., Roseff, R.L., 1986. Citrus Fruit and Their Products: Analysis and Technology. Marcel Dekker, NY, USA.

Torrestiana-Sanchez, B., Balderas-Luna, L., Brito-De la Fuente, E., Lencki, R.W., 2007. The use of membrane-assisted precipitation for the concentration of xanthan gum. J. Membr. Sci. 294, 84–92.

Tripoli, E., La Guardia, M., Giammanco, S., Di Majo, D., Giammanco, M., 2007. Citrus flavonoids: molecular structure, biological activity and nutritional properties. A review. Food Chem. 104, 466–479.

Vanaclocha, B., Cañigueral, S., 2003. Fitoterapia, 4th ed. Elsevier-Masson, Barcelona, España.

Wang, D., Li, K., Teo, W.K., 1999. Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes. J. Membr. Sci. 163, 211–220.

Wenzel, R.N., 1949. Surface roughness and contact angle. J. Phys. Colloid Chem. 53, 1466–1467.

Zhao, R., Yan, Y., Li, M., Yan, H., 2008. Selective adsorption of tea polyphenols from aqueous solution of the mixture with caffeine on macroporous crosslinked poly(N-vinyl-2-pyrrolidinone). React. Funct. Polym. 68, 768–774.