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Impact of structural and textural membrane properties on lemon juice clarification

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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.

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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

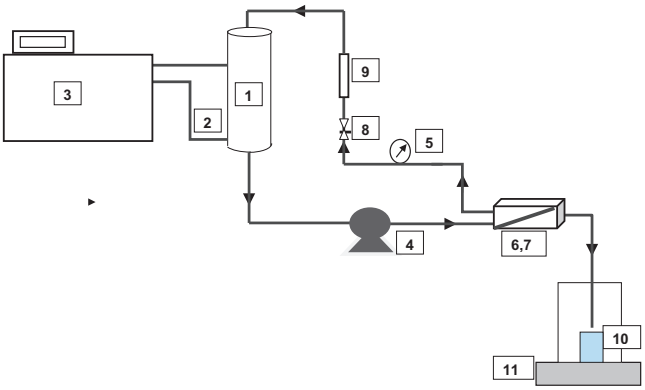

Fig. 1 – Permeability equipment: 1 – Liquid under study. 2 – Thermostabilized reservoir. 3 – Thermostatic bath. 4 – Peristaltic pump. 5 – Pressure gauge. 6 – Permeation cell Minitan-S. 7 – Membrane. 8 – Needle valve. 9 – Flowmeter. 10 – Sampling glass. 11 – Analytical balance.