Vegetable oil degumming with polyimide and polyvinylidenefluoride ultrafiltration membranes

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Abstract: The removal of phospholipids ('degumming') is the first step in the process of refining crude vegetable oil. Membrane separation has been often proposed as an alternative to the conventional procedure (water degumming). Until now, the instability of polymeric membranes in organic solvents has been the major obstacle in applying this technique. In this work, a local synthesized polyvinylidenefluoride (PVDF) and a commercial polyimide (PI) membrane were evaluated for their flux and rejection properties during degumming of soybean oil in a laboratory-scale cross-flow ultrafiltration cell. Degumming experiments were done at different temperatures and feed flows, keeping constant both the feed concentration and the transmembrane pressure. PVDF and PI membranes gave selectivity values and permeate color that did not differ significantly from each other. Retention coefficients larger than 98% were obtained in all cases. In every experiment, a decline in permeate flux with time occurred at the beginning of the degumming process. By increasing the feed rate, a higher permeate flux was obtained. The results show that the PVDF membrane had a higher productivity than the PI one.
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INTRODUCTION

Membrane processes, such as ultrafiltration (UF), are widely used as an effective separation technology.[1] The major advantage of this technology is the use of low operating temperatures, which results in lower operating cost and minimal damage to thermally unstable products. Membrane separation processes are scarcely used in the oilseed industry. The main reasons for this have been poor membrane stability in organic solvents (mainly hexane) and low permeate flux due to high oil viscosity.[2]

From all possible applications of membrane technology to the processing of vegetable oils,[3–8] degumming is an operation claimed to be 'mature', but some points have not been reported and/or the information given is confusing; the characteristic of the membrane is one of these.

In an earlier work, different types of polymeric membranes were checked to degum a crude oil/hexane miscella in a stirred dead-end ultrafiltration cell.[2] PVDF membranes gave promising results regarding their stability in solvent and permeate flux values.

It was found that permeate flux decreased continuously as permeation proceeded. At the beginning of the permeation process, the flux decline was much more pronounced than it was at longer times. These results indicate that degumming of oil/hexane miscella is subjected to a severe membrane fouling process. Similar behavior was observed in a recent study using polyvinylidenefluoride (PVDF) and polyimide (PI) membranes in the same ultrafiltration cell.[9] The flow arrangement used to conduct the experiments in the above-mentioned studies benefited such fouling.

Membrane fouling can be reduced and/or controlled using a tangential flow ultrafiltration cell. This device has some advantages over the dead-end design, mainly due to its capacity to reduce the formation of a concentration polarization layer, thereby decreasing the levels of fouling and pore blocking.

The goal of this work was to determine the performance of PVDF and PI membranes in a cross-flow arrangement during the degumming of soybean oil/hexane miscella. Under these conditions it is expected that surface fouling will be minimized and the membrane performance decided mainly by the membrane structure and membrane–solvent interaction effects; therefore the comparison between

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both membranes tested will be less dependent on the process itself than in a dead-end flow arrangement. The membrane performance was evaluated in terms of permeate flux, phospholipid retention and color reduction. The effects of flow velocity and process temperature on the membrane behavior are analyzed. Pore size distribution, and affinity between solvent and membrane material are assessed in order to explain the differences in flux between the membranes.

EXPERIMENTAL PROCEDURE
Membranes
PI ultrafiltration membrane, with a molecular weight cut-off (MWCO) of 20 000, was acquired from Koch Membrane System (MPS-U20-S, Wilmington, MA, USA). PVDF membrane, with an MWCO of 6000, was synthesized in our laboratory by the phase inversion technique.[2] The characterization was done using an aqueous dextran solution, as previously reported.[2]

Experimental equipment
The tangential ultrafiltration device used is shown in Fig 1. The feed solution was pumped continuously through the cross-flow cell from a thermostatic reservoir by means of a centrifugal pump at a predetermined cross-flow velocity, v, and transmembrane pressure, ΔP. These operating conditions were maintained by two needle valves. The transmembrane pressure was taken as the average value of the pressure difference at the inlet and outlet of the membrane cell.

The membrane was clamped between the two hemi-cells. On the membrane feed side there was one duct of rectangular section (10^{-3} m high $\times$ 6 $\times$ 10^{-3} m wide $\times$ 0.115 m long). The resulting channel hydraulic diameter (d_h) was 1.97×10^{-3} m and the effective membrane area was 6.9×10^{-3} m^2.

Pure solvent permeability test
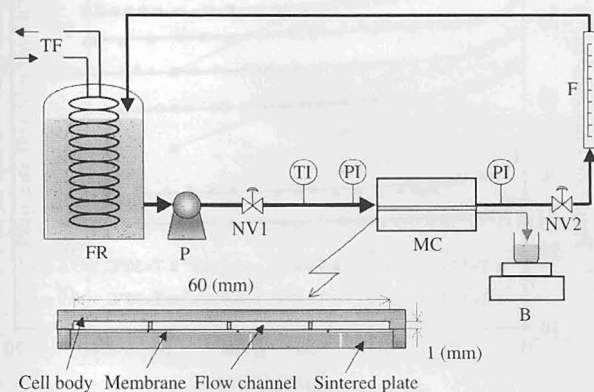In order to investigate the effect of solvent on membrane structure, the experimental equipment described in the previous paragraph was used to determine the membrane permeability to pure water and pure hexane. The pure liquid permeate fluxes were measured as a function of the applied transmembrane pressure (0.05 MPa $< \Delta P <$ 0.3 MPa) at different values of cross-flow velocity (0.9 m s^{-1} $< v <$ 1.6 m s^{-1}) and temperature (20 °C $< T <$ 50 °C). Before carrying out hexane permeability measurements, the membranes were soaked in solvents of decreasing polarity to reduce the solvent effect on membrane structure.[9]

Pore size distribution
In order to evaluate the normalized membrane pore size distribution function, f_D, solute retention tests were performed by feeding the permeation module with an aqueous solution of a polyethyleneglycol (PEG) mixture, following the procedure described elsewhere.[10] PEGs of different molecular weights were obtained from Fluka (Sigma-Aldrich, BA, Argentina). The concentration of PEG with molecular weight $M_{w,i}$ in feed, $C_{f,i}^{PEG}$, and permeate, $C_{p,i}^{PEG}$, were measured using HPLC equipment from Gilson (Walnut Creek, CA, USA) with a Varian TSK 3000 SW column coupled with a refractive index detector. If the PEG molecular weight (i) is related to its molecular size by $M_{w,i} \propto r_{p,i}^2$ and a sieve mechanism to explain the pore retention capability is assumed, the cumulative pore size distribution, $F(r_p)$, can be related to data from retention tests through an expression like:[10]

$$F(r_p) = \frac{(1 - R_i^a)}{(1 - C_{p,i}^a)} = \left[1 + \left(\frac{r_p}{B} \right)^C \right]^{-1} \quad (1)$$

with R_i^a, the cumulative retention coefficient, given by:

$$R_i^a = 1 - \frac{C_{p,i}^a}{C_{m,i}^a} \quad (2)$$

where $C_{p,i}^a = \sum_{k=0}^{i} C_{p,k}$ and $C_{m,i}^a = \sum_{k=0}^{i} C_{m,k}$ are the concentrations of PEG with molecular weight equal to or less than $M_{w,i}$ in the permeate and on the membrane side, respectively. B and C are constants determined by fitting the experimental data to eqn (1). To evaluate the retention coefficient by eqn (2), different low pressure retention tests were done and the results extrapolated to zero pressure. Under these extrapolated conditions, the membrane side concentration (C_m) could be considered as identical to the feed concentration.[10] The normalized pore size distribution function, f_D, was evaluated as:

$$f_D = K \frac{dF(r_p)}{dr_p} \quad (3)$$

where K is a normalization constant.

Degumming experiments
Before use, membranes were conditioned with solvents of decreasing polarity according to the procedure mentioned previously. Immediately after this procedure, a membrane was put into the cell

Figure 1. Experimental set-up, with internal details of UF cell. B: Balance, F: flowmeter, FR: feed reservoir, MC: membrane cell, NV: needle valve, P: pump, PI: pressure indicator, TI: temperature indicator, TF: thermostatic fluid.

and the pump was started. All trials were performed using a commercial grade hexane/soybean oil mixture (75/25 w/w). Permeate flux was measured as a function of time at given values of applied transmembrane pressure, temperature and flow velocity.

Permeate flow was measured by timing and weighing with a precision balance. Permeate and retentate were sent continuously back to the feed vessel to keep the feed concentration constant. The phospholipid concentrations in the feed, C_f^{ph}, and permeate, C_p^{ph}, were measured to determine the membrane retention coefficient (%R) defined as:

$$\%R = 100 \left(1 - \frac{C_p^{ph}}{C_f^{ph}} \right) \qquad (4)$$

After each trial, the membrane was washed with hexane until the original pure hexane flux was restored.

Analytical methods

Phosphorus contents of the feed and permeate were measured following AOCS method Ca 12–55.[11] Total phospholipid concentration was evaluated as 30 times the phosphorus content. The color of the feed and permeate was determined using an automated tintometer (Lovibond tintometer, Model PFX190, Salisbury, UK). Contact angle measurements were done using a Micromeritics Contact Anglometer (Model 1501).

RESULTS AND DISCUSSION
Membrane selectivity

Table 1 reports values of phospholipid retention coefficient (%R) as defined in eqn (4). While PVDF showed a slightly better selectivity than PI, both membranes gave a high retention of phospholipid. Temperature affected the membrane selectivity inversely while flow velocity had no noticeable effect on this parameter.

Permeate color

During membrane degumming some colored substances were trapped inside the reverse micelles formed by phospholipids and removed with the retentate,[3]

Table 1. Retention coefficient and permeate color during degumming of hexane–soybean oil mixtures

T(°C)	v(m s^{-1})	Retention coefficient (% R)		Permeate color	
		PVDF	PI	PVDF	PI
30	0.9	99.7	99.7	0.2R 45Y	0.1R 38Y
	1.6	99.7	98.9	0.2R 45Y	0.2R 34Y
40	0.9	99.6	98.5	0.2R 45Y	0.2R 45Y
	1.6	99.3	98.1	0.1R 45Y	0.1R 45Y
50	0.9	98.3	97.8	0.2R 45Y	0.2R 45Y
	1.6	99.1	97.9	0.1R 45Y	0.2R 45Y

Feed color: 0.5R 50Y (R: red; Y: yellow).

giving a less colored permeate as compared with the feed. Values of permeate and feed color are given in Table 1. In all cases, the red component of permeate color was notably reduced with respect to that of the feed. This reduction was not so obvious for the yellow component.

Miscella permeate flux

The PVDF membrane allowed higher permeate fluxes than the PI membrane under all the experimental conditions checked in this work. Figures 2 and 3 show how permeate flux changed with time during degumming trials at different temperatures and feed flows for the PVDF and PI membranes respectively. In all cases, transmembrane pressure difference was kept at 2.7 bar. Both membranes showed a slight
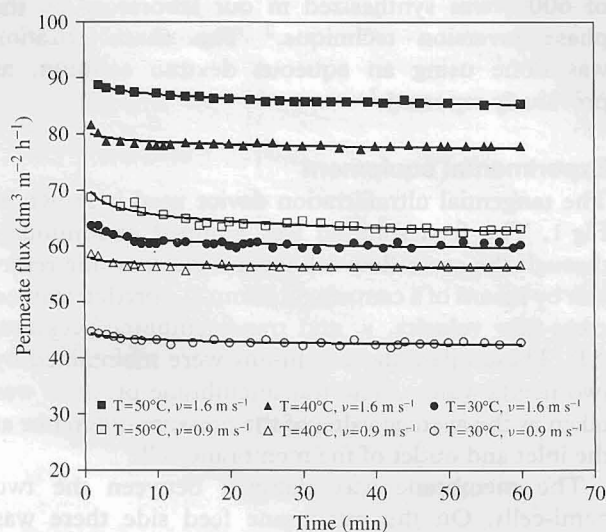
Figure 2. Permeate flux through PVDF membrane plotted as a function of time at different temperatures and cross-flow velocities, during degumming of a crude soybean oil/hexane mixture. Lines represent the best exponential fit to the experimental data. $\Delta P = 2.7$ bar.

Figure 3. Permeate flux through PI membrane plotted as a function of time at different temperatures and cross-flow velocities, during degumming of a crude soybean oil/hexane mixture. Lines represent the best exponential fit to the experimental data. $\Delta P = 2.7$ bar.
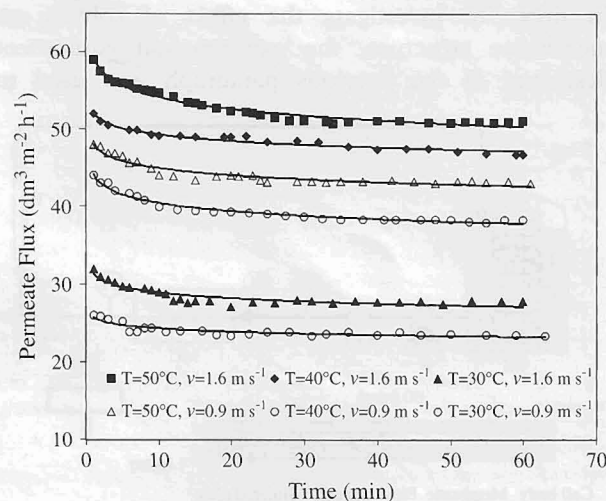
flux decline at the beginning of the permeation process and after that, permeate flux remained almost constant for the period considered in the assays. In all cases, the permeate flux increased with fluid velocity. These results suggest that the observed flux behavior is mainly determined by a concentration polarization layer whose thickness decreases with increasing fluid velocity and an initial fouling process that is responsible for the initial flux decline.

The permeate flux observed at $t = 60$ min, $\mathcal{J}_v^*$, was used to compare the permeability properties of the tested membranes. As the temperature increased, $\mathcal{J}_v^*$ increased, as is shown in Fig 4. Since the behavior of both membranes was similar, it was inferred that the increase in $\mathcal{J}_v^*$ was due to a decrease in fluid viscosity affecting both membranes, affecting the extent of the concentration polarization layer and the membrane internal flow resistance.

While both membranes had about the same phospholipid rejection coefficient, they showed a great difference in permeate flux, PVDF being almost twice as permeable as PI. These results cannot be explained in terms of their difference in MWCO values alone but the solvent–membrane interactions have to be considered.

Pore size distribution

Figure 5 shows the normalized differential pore size distribution of PVDF and PI membranes obtained from eqn (3). It is clear from this figure that both membranes had very similar mean pore radii, $\langle r_p \rangle$, (PVDF 27.2 Å and PI 28.9 Å). The PI membrane shows a long-tailed pore size distribution which is responsible for the high cut-off (20 000) compared with that of the PVDF membrane (6000).

Effect of solvent on membrane properties

In order to verify the solvent effect on membrane behavior and to explain the observed differences in
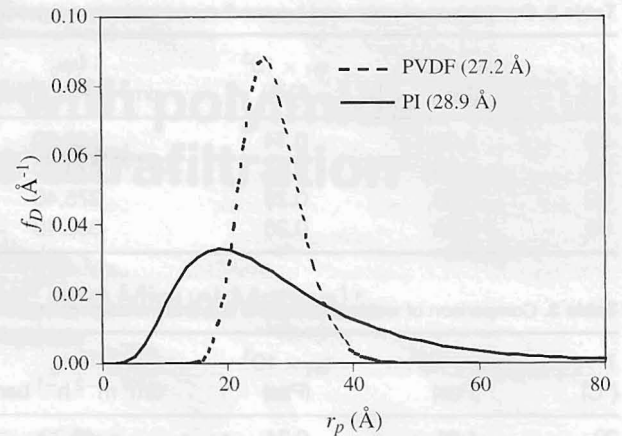
Figure 5. Normalized differential pore size distribution, f_D, for PVDF and PI membranes.

permeate flux, the experimental results from pore size distribution and pure water and pure hexane permeability were considered. In all cases a linear dependence of pure hexane and pure water permeate flux, $\mathcal{J}_{H,0}$ and $\mathcal{J}_{W,0}$, on ΔP was observed. It was found that $\mathcal{J}_{H,0}$ and $\mathcal{J}_{W,0}$ are not affected by flow velocity. The hexane and water permeabilities, $L_{H,0}$ and $L_{W,0}$ respectively, are defined in terms of the applied transmembrane pressure and observed fluxes as:

$$L_{i,0} = \frac{\mathcal{J}_{i,0}}{\Delta P} \qquad (5)$$

where i can take the values H or W, depending on whether eqn (5) is applied to hexane or water, respectively. In the absence of swelling effects, the solvent transport mechanism prevalent in the UF membranes tested should be convective in nature, therefore a Hagen–Poiseuille type equation can be used to relate $L_{i,0}$ to membrane properties as:[12]

$$L_{i,0} = \frac{\varepsilon \langle r_p \rangle^2}{8 \eta_i \tau \lambda} = \frac{1}{\eta_0 R_m^i} \qquad (6)$$

where η_i is the solvent dynamic viscosity, λ, $\langle r_p \rangle$, ε and τ are the pore length, mean pore radius, surface porosity and pore tortuosity of the membrane respectively. $R_m^i = (8 \tau \lambda)/(\varepsilon \langle r_p \rangle^2)$ is the intrinsic membrane resistance to solvent i.

Membrane permeabilities and intrinsic resistance values of PVDF and PI membranes at different temperatures in the range $20\,°C < T < 50\,°C$ are summarized in Tables 2 and 3 respectively. These values were obtained from eqns (5) and (6). In these tables, viscosity values for water and hexane[13] are also shown. The average R_m^i values in the temperature range mentioned for both tested membranes are $R_m^w|_{PVDF} = 2.06 \times 10^{12}$, $R_m^H|_{PVDF} = 12.6 \times 10^{12}$, $R_m^w|_{PI} = 8.14 \times 10^{12}$ and $R_m^H|_{PI} = 66.18 \times 10^{12}$ (m^{-1}), ie R_m^i values for the PI membrane are about five times those for the PVDF one. Given their very similar mean pore sizes (see Fig 5) it is clear that the two membranes should have different porosities, tortuosities, thicknesses and/or support structures.
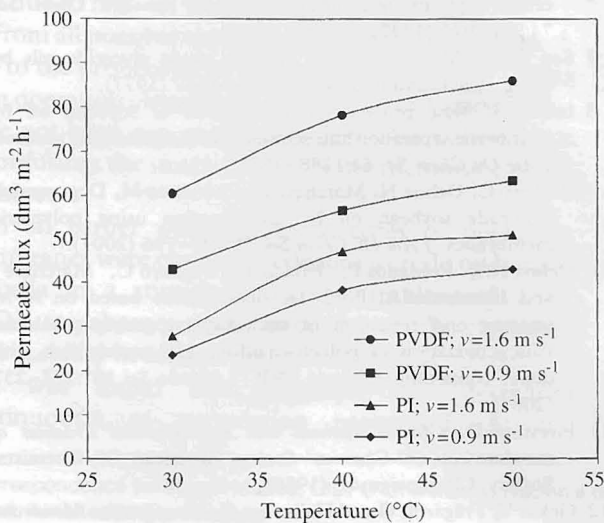
Figure 4. Permeate flux through PVDF and PI membranes plotted against temperature at cross-flow velocity during degumming of a crude soybean oil/hexane mixture. Lines represent the best exponential fit to the experimental data. $\Delta P = 2.7$ bar.

Table 2. Comparison of water and hexane flux and intrinsic resistance values at different temperatures for PVDF membrane

T (°C)	$\eta_W \times 10^3$ (Pa s)	$\eta_H \times 10^3$ (Pa s)	L_{W_0} dm^3 m^{-2} h^{-1} bar^{-1}	L_{H_0} dm^3 m^{-2} h^{-1} bar^{-1}	$R_m^w \times 10^{-12}$ (m^{-1})	$R_m^H \times 10^{-12}$ (m^{-1})
20	1.01	0.34	160.30	79.50	2.20	13.31
30	0.80	0.31	215.60	90.57	2.09	12.81
40	0.66	0.28	275.40	104.18	1.98	12.33
50	0.55	0.26	335.40	116.30	1.95	11.09

Table 3. Comparison of water and hexane flux and intrinsic resistance values at different temperatures for PI membrane

T (°C)	$\eta_W \times 10^3$ (Pa s)	$\eta_H \times 10^3$ (Pa s)	L_{W_0} dm^3 m^{-2} h^{-1} bar^{-1}	L_{H_0} dm^3 m^{-2} h^{-1} bar^{-1}	$R_m^w \times 10^{-12}$ (m^{-1})	$R_m^H \times 10^{-12}$ (m^{-1})
20	1.01	0.34	40.22	15.01	8.86	70.48
30	0.80	0.31	53.23	17.10	8.40	67.86
40	0.66	0.28	69.81	19.50	7.81	65.88
50	0.55	0.26	87.20	22.87	7.50	60.49

As $\langle r_p \rangle$ is much larger than the solvent molecular size, transport through the membrane should be controlled by solvent viscosity and the intrinsic membrane resistance should be unaffected by the operating parameters. However, the average intrinsic resistance values show that $R_m^H|_{PVDF} \cong 6R_m^w|_{PVDF}$ and $R_m^H|_{PI} \cong 8R_m^w|_{PI}$. These results confirm that there is a significant change of the membrane structure (swelling) when it is put in contact with hexane, a non-polar solvent.

The solvent–membrane affinity was estimated by contact angle measurements. Contact angle values of 70° and 43° for water–PVDF and water–PI systems, respectively, were measured. These values confirm that the PI membrane has a more hydrophilic character than the PVDF one, supporting the higher difference between R_m^H and R_m^w for the PI membrane. It needs to be pointed out that hexane wetted both membranes completely and because of that, contact angle could not be measured.

CONCLUSIONS

A local by produced PVDF membrane and a commercial PI-based membrane were used to remove phospholipids from a hexane–vegetable oil mixture. The results showed that, although both membranes had a high selectivity for the separation of phospholipids, PVDF gave much higher permeate fluxes, making this membrane more acceptable for industrial use. It is clear from the results that a pure viscous flow mechanism cannot explain the transport properties of solvents through the membranes tested in this work. It seems reasonable to suppose that membrane structure and solvent–membrane affinity effects combine to determine the higher hexane flux through the PVDF membrane as compared with the PI one.

ACKNOWLEDGEMENTS

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