

Degumming of Crude Soybean Oil by Ultrafiltration Using Polymeric Membranes

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ABSTRACT: In this study, the ability of two ultrafiltration polymeric membranes to perform the degumming of a crude soybean oil/hexane mixture is tested. The performance of both membranes is defined in terms of their permeation flux, permeate color, and rejection of phospholipids. One of the membranes was synthesized in our laboratories from polyvinylidene fluoride (PVDF); the other one is a commercially available membrane made of polyimide. The degumming experiments were done in a stirred dead-end ultrafiltration cell pressurized with N₂. Results show that tested membranes are suitable for removing phospholipids from the crude oil/hexane miscella in the range of temperature and transmembrane pressure utilized in this work. Both membranes have high selectivity regarding phospholipids and produce a moderate reduction in permeate color. The PVDF membrane gives permeate fluxes up to three-fold larger than those obtained with polyimide membrane at the same operational conditions, making the former more suitable for use at industrial scale.

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KEY WORDS: Membrane degumming, membrane synthesis, vegetable oil.

Crude vegetable oils consist mainly of triglycerides or neutral oil with fat-soluble and suspended impurities. The amounts of these impurities change with oil source, geographical and seasonal factors, and extraction process (1). Nowadays, crude vegetable oils are obtained more frequently by crushing oilseeds followed by solvent extraction.

Purification of the neutral oil portion is the major goal of the refining process. The nontriglyceride fraction contains variable quantities of such impurities as free fatty acid, phospholipids (gums), color pigments, metal complexes, sterols, waxes, carbohydrates, proteins, water, and dirt (2). Most of these impurities are detrimental to the quality of the finished product and must be removed from the neutral oil during processing.

The removal of phospholipids (“degumming”) is the first step of crude vegetable oil refining process. In so-called water degumming, crude oil is treated with water, salt solutions, or dilute acid to remove phospholipids. This process changes phosphatides into hydrated gums, which are insoluble in oil.

Such gums are separated from the oil by filtering, settling, or centrifugal action (3). In this procedure, a considerable loss of neutral oil occurs and a large amount of wastewater is produced, and the energy consumption is fairly large.

An alternative means to separate phospholipids from neutral oil is the use of membrane separation processes. In non-polar media like hexane or neutral oil, phospholipid molecules tend to form reverse micelles with an average molecular weight (MW) of 20,000 daltons or more (4). This large MW enables the separation of phospholipids from either triglycerides (MW ~ 800 daltons) or triglyceride/hexane mixtures (miscella) by ultrafiltration using appropriate membranes. The advantages of this technology are that it is simple, it can be done at ambient temperature if required, and it demands a small amount of energy. Further, since no chemicals are necessary to accomplish the separation, there is no wastewater generation (5,6).

Membrane processing has been applied to remove phospholipids from crude oil/hexane mixtures (7–9) as well as from crude oil itself without the addition of organic solvent (10). The last option seems to be less suitable because of the low permeate flow obtained as a consequence of high oil viscosity.

Degumming crude oil/hexane miscella with membranes produces permeate and retentate fractions containing mostly triglycerides and phospholipids, respectively. Colored materials, some free fatty acids, and other impurities are trapped by the reverse micelles and are removed with the retentate fraction along with most of the phospholipids.

Until now, major limitations for membrane degumming have been the poor membrane stability in organic solvent and the low permeate flow compared to the scale of the oil processing industry. Recent results (11) have shown that membranes obtained from polyvinylidene fluoride (PVDF) have good stability in hexane and acceptable permeate flux.

The objective of this work was to evaluate the efficiency of membrane technology under different process conditions for the degumming of crude soybean oil/hexane miscella using two polymeric membranes, a commercially available membrane made of polyimide (PI) and a PVDF-based membrane produced in our laboratories.

MATERIALS AND METHODS

Membranes. Two different membranes were utilized during the trials. One of them, a commercially available ultrafiltration

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membrane made of PI, was obtained from a worldwide membrane supplier (membrane identification: MPS-U20-S, Koch Membrane System Inc., Wilmington, MA). The other one, identified in this work as LM-1, was synthesized in our laboratory from PVDF as described elsewhere (11). Their MW cut-offs (MWCO) were 20,000 and 6,000 daltons, respectively.

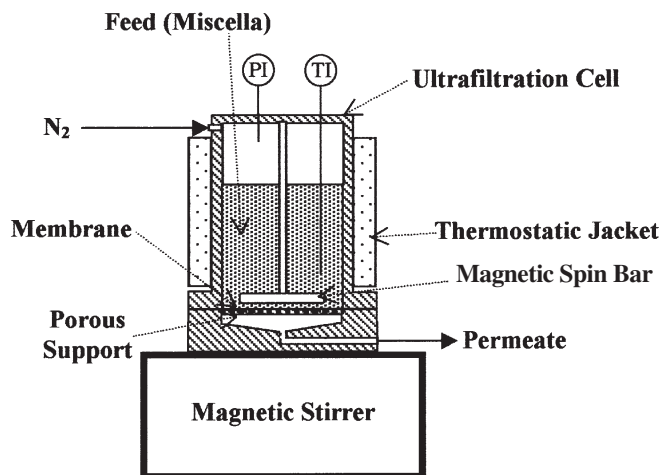
Miscella. Degumming experiments were carried out with a crude soybean oil/hexane miscella. The miscella was obtained by mixing 25% (w/w) of crude soybean oil (obtained from a local oilseed crushing plant) with hexane (industrial grade).

Membrane apparatus. Scheme 1 is a diagram of the experimental setup, which consisted of a stirred dead-end ultrafiltration cell, a magnetic stirrer, and a nitrogen cylinder to provide the driving force (pressure) for permeation (PI, pressure indicator; TI, temperature indicator). The cell's capacity was 400 mL; it allows fitting plane membranes with an effective membrane area of $2.8 \times 10^{-3} \text{ m}^2$. Membranes were supported on a sintered stainless steel disk. Continuous agitation was provided just above the membrane surface by a magnetic spin bar suspended from the cell top and driven by an external magnetic stirrer. The nitrogen cylinder was connected to the top of the test cell. To collect the permeate, a conduit in the bottom plate was provided.

Degumming experiments. As a way to minimize the solvent effect on the membrane structure during degumming, both membranes were soaked in solvents of decreasing polarity (50:50 solution of water/isopropyl alcohol; 50:50 solution of isopropyl alcohol/hexane; and finally pure hexane) for periods of 48 h. After this procedure, the cell was charged with hexane, and pure solvent flux through the membrane was measured as a function of the applied pressure (from 0.5 to 6 bar) at 25, 35, and 45°C. These results were used to evaluate the membrane permeability to hexane, L_h , defined as:

$$L_h = J_h / \Delta P \quad [1]$$

where J_h is the permeate flux expressed as $\text{L}/\text{m}^2\text{h}$, and ΔP is the applied transmembrane pressure, measured in bars.



SCHEME 1

The degumming experiments were carried out with the miscella immediately after the pure solvent test. Cell pressure and fluid temperature were varied from 2 to 6 bars and 25 to 45°C, respectively. All experiments were done at a constant rotation speed of the spin bar (250 rpm). In all cases, 300 mL miscella were charged into the cell initially; each trial was continued until permeate volume collected at the bottom conduit amount to 180 mL. The concentrations of phospholipid in feed and permeate were measured to determine the membrane retention coefficient, %R, defined as:

$$\%R = (1 - C_p/C_f) \times 100 \quad [2]$$

where C_p and C_f are phospholipid concentration in permeate and feed, respectively. After each trial, the membrane was thoroughly cleaned with hexane flowing counter to normal sense. Before starting a new experiment, the membrane was checked to see that it yielded the original pure hexane permeate flux.

Analytical methods. Phosphorus content of crude oil was measured following American Oil Chemists' Society Method Ca 12-55 (12). Total phospholipid concentration was evaluated as 30 times the phosphorus content. Color of feed, permeate, and retentate were determined using an automated tintometer (model PFX190, Lovibond tintometer, Salisbury, United Kingdom).

RESULTS AND DISCUSSION

Permeate flux. LM-1 membrane allows larger pure hexane fluxes than MP-U20-S at the same transmembrane pressure in the whole temperature range analyzed. The effect of temperature on pure hexane flux on MPS-U20-S is minimal. Measured data show that pure hexane flux increased almost linearly with pressure when it was raised from 0.5 to 3 bar, indicating that the membrane structure remains unaltered by pressure in the studied pressure range. Table 1 shows L_h values obtained from Equation 1 by fitting a straight line to the experimental J_h vs. ΔP data.

During degumming experiments, the permeate flux decreased with process time in all cases. Permeate flux decreases more noticeably at short times, suggesting that fouling of the membranes is an important factor at the beginning of the permeation process. The flux decline is much less pronounced at long times than it is initially; this tendency implies that a gel layer may be affecting the membrane at the final stage (13). Figures 1 and 2 show the flux of the fluid mixtures, J , permeated through MPS-U20-S and LM-1 membranes, respectively, as a function of time at different pressures. In all cases, a sharp decline in permeate flux is observed at the beginning of the process. The LM-1 membrane gave higher fluxes at all times and pressures than the MPS-U20-S membrane. For both membranes, but notably for LM-1, a greater pressure effect is detected at low pressure values. [The effect of pressure on permeate flux can be obtained from Fig. 3 by plotting J (evaluated as $L \cdot \Delta P$ from Eq. 1) vs. ΔP . In this plot (data not shown) permeate flux levels off as pressure increases. The effect is more noticeable in the case of

TABLE 1
Membrane Performance During Degumming of Crude Soybean Oil/Hexane Miscella^a

Membrane	Temperature (°C)	L_h (L/h·m ² ·bar)	Pressure (bar)	C_p (ppm)	%R ^b	Color	
						Permeate	Retentate
MPS-U20-S	25	14.6	2	5	99.6	0.3R65Y	2.1R65Y
			4	2.2	99.8	0.1R60Y	2.3R65Y
			6	2.2	99.8	0.1R45Y	3.0R65Y
	35	18.8	2	9	99.3	0.3R65Y	2.0R65Y
			4	2.2	99.8	0.3R55Y	1.9R65Y
			6	2.2	99.8	0.2R50Y	2.3R65Y
	45	20.0	2	2.2	99.8	0.3R65Y	2.8R65Y
			4	2.2	99.8	0.5R65Y	2.0R65Y
			6	6	99.6	0.2R60Y	2.1R65Y
LM-1	25	89.9	2	10	99.2	0.5R65Y	2.1R65Y
			4	1.6	99.9	0.4R65Y	2.9R65Y
			6	7	99.5	0.2R65Y	2.9R65Y
	35	95.1	2	2.2	99.8	0.5R65Y	2.1R65Y
			4	1.6	99.9	0.4R65Y	3.2R65Y
			6	1.6	99.9	0.3R65Y	3.6R65Y
	45	117.4	2	2.2	99.8	0.6R65Y	2.8R65Y
			4	12	99.1	0.4R65R	2.9R65Y
			6	6	99.6	0.4R65Y	4.2R65Y

^aColor of initial miscella: 1.7R65Y. Crude oil characteristics: phospholipid content (C_p) = 1297 ppm; free fatty acid (expressed as oleic acid): 0.45; Color: 5.1R65Y (R: Red; Y: Yellow). C_p = phospholipid content of permeate.

^bEquation 2.

the LM-1 membrane than the MPS-U20-S.] Thus, permeate flux increased more rapidly when pressure was raised from 2 to 4 bar than when it was changed from 4 to 6 bar. These results suggest that at higher pressures, concentration polarization phenomena start to play an important role in the permeation process, making the permeate flux less sensitive to the applied transmembrane pressure. So, at high pressure, a layer of rejected mole-

cules (gel-polarized layer) deposits on the membrane surface, and the flow process is highly dependent on the consolidation of this layer (13), but it is not very much influenced by pressure. In Figure 1, data at 4 and 6 bars show zigzag. This may be due to the stirrer, whereby excessive mixing could bring nitrogen bubbles to the membrane surface. Figure 3 shows permeability values, L , as a function of pressure at different temperatures,

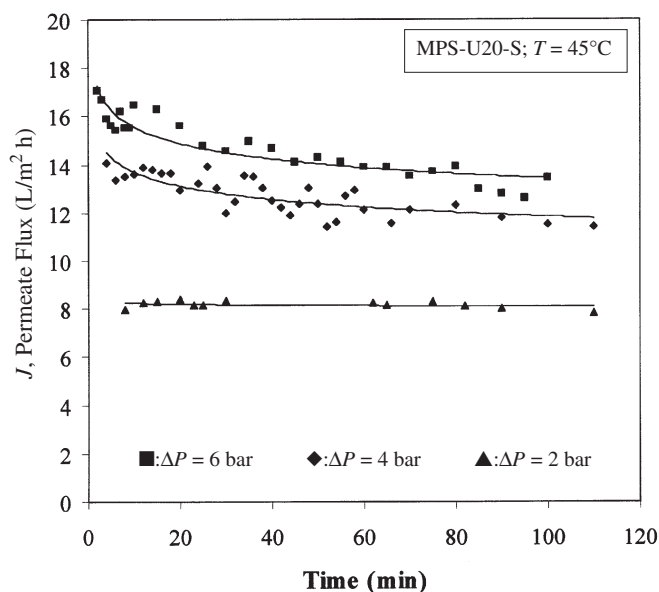


FIG. 1. Permeate flux (J) through membrane MPS-U20-S (see the Materials and Methods section) plotted as a function of time during degumming of crude soybean oil/hexane miscella. Lines represent the best exponential fit to experimental data (dots).

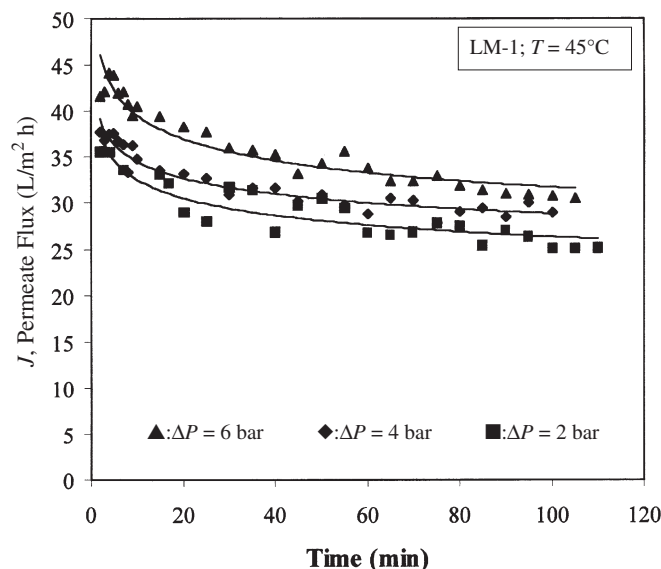


FIG. 2. Permeate flux (J) through membrane LM-1 (see the Materials and Methods section) plotted as a function of time during degumming of crude soybean oil/hexane miscella. Lines represent the best exponential fit to experimental data (dots).

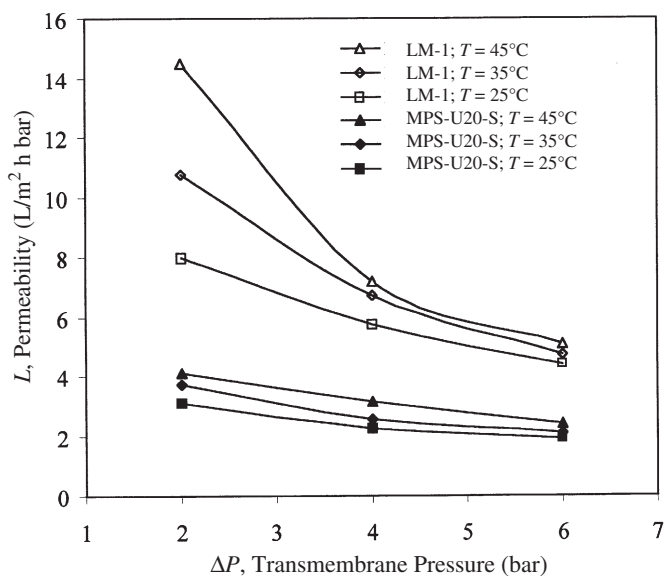


FIG. 3. Membrane permeability plotted against transmembrane pressure.

evaluated according to Equation 1, using the permeate flow, J , at $t = 100$ min in all cases. As temperature increases, so does permeate flux, since higher temperature reduces the viscosity of permeate fluid.

Color. During degumming some colored substances are trapped inside the reverse micelles formed by phospholipids and removed with retentate. In Table 1, color of feed, permeate, and retentate are shown. The red component of permeate, color was reduced significantly in all cases with respect to the red color of feed. Yellow color remains mostly unaffected by the process. MPS-U20-S membrane yielded a slightly better reduction than LM-1.

Selectivity. The membrane selectivity was assessed by measuring the phospholipid retention coefficient, %R, as given by Equation 2. Table 1 shows %R values for both tested membranes. In all cases, tested membranes have shown high selectivity, resulting in %R greater than 99%. Temperature and pressure have no noticeable effect on these values. The %R as well as color were determined on samples taken from the whole permeate and retentate volumes.

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