Membrane Degumming of Crude Soybean and Rapeseed Oils

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ABSTRACT: Membrane separation in edible oil processing is a potential area for energy savings. However, technical and operating-cost-related barriers have impeded the successful application of membrane separation in food processing. Studies were undertaken with soybean and rapeseed oils in a magnetically stirred flat-membrane batch cell with two types of composite polymeric membranes at 3 MPa pressure and at a constant temperature of 40°C. The membranes were NTGS-1100 and NTGS-2100, and used silicon as the active layer and polysulfone and polyimide as support layers, respectively. The membrane selectively rejected phospholipids, the content being less than 240 mg/kg in the permeate without any pretreatment or dilution of crude oil with organic solvent. Long-term studies up to 97 days with soybean oil at two different pressures, 2 and 3 MPa, showed that the rejection of phosphatides was above 96% in most permeates. The permeate flux remained nearly constant but must be improved.
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KEY WORDS: Degumming, microfiltration, nonporous membrane, phospholipids, phosphorus, polyethylene membrane, polymeric composite membrane, rapeseed oil, soybean oil.

Degumming is the first step of crude vegetable oil refining, in which phospholipids are removed that otherwise would act as emulsifying agents, lead to loss of neutral oil, and result in a low-grade finished product (1). Oilseeds are invariably subjected to enzymatic action due to the various factors encountered, from the stages of harvesting to processing, that lead to the formation of calcium and magnesium salts of phosphatidic acid, ethanolamine, and inositol compounds. Several processes have been developed to lower the phosphatide content of oils and to increase the efficiency of the degumming process.

In conventional processing, water or dilute acid is used during the degumming step. In the water-degumming process, phospholipids are precipitated by hydration, followed by agitation and centrifugation. The phospholipid content of an oil of average quality is reduced to a range between 1800 and 6000 mg/kg, and the corresponding phosphorus content is 60–200 mg/kg (2). Acid degumming, in which the hydratability of salts of phosphatidic acid is increased by addition of either phosphoric or citric acid, lowers the phospholipid content to about 1500 mg/kg (3). Super-degumming, a patented process widely used in the industry, produces an oil with a maximum phospholipid content of 900 mg/kg (4). The amount of acid used in the acid-degumming process varies between 0.05 and 0.2% of the oil weight and is even as high as 0.5% in oils that contain an initial phospholipid content of 6000 mg/kg and higher.

Membrane processing seems to be a simple and promising tool to refine vegetable oils, due to low energy consumption, ambient temperature operation, no addition of chemicals, and retention of nutrients and other desirable components (5,6). At the present time large amounts of vegetable oils are being produced by expression, followed by solvent extraction. Expeller-pressed oil is three times higher in quantity than solvent-extracted oil. Hence, the use of membranes for degumming appears to be more appropriate with crude oil than hexane–oil miscella, which was used by earlier workers (7–10).

The pressure-driven membrane processes are classified as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration (11). Micelle-enhanced ultrafiltration (MEUF) is a recently developed technique, in which surfactants are used to adsorb undesirable components electrostatically from the feed, thus forming larger complex aggregates of about 20 kDa that are impermeable to the membrane pores. German, Japanese, and American workers have successfully applied this technique for degumming hexane–oil miscella (7–10). Phospholipids in vegetable oils act as surfactants, and MEUF does not require additional surfactant. With this background, the prime objective of this study was to evaluate the efficiency of the membrane process for degumming crude soybean and rapeseed oils without the addition of organic solvents.

EXPERIMENTAL PROCEDURES

Samples. Samples of soybean and rapeseed oils (crude, deodorized, and oils from different stages of refining) were obtained through the courtesy of M/s Nippon Lever, Shimidzu, Japan.

Membranes. Polyethylene microfiltration membranes with pore sizes of 0.01, 0.02, and 0.03 μm were kindly supplied by M/s Tonen Chemical Corporation, Kawasaki, Japan. They

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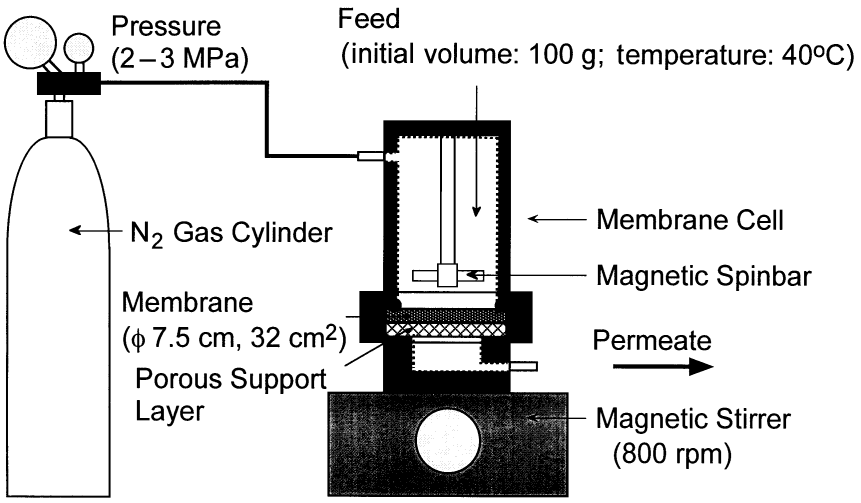

FIG. 1. Membrane apparatus and operating conditions.

were designated as PE-10, PE-20, and PE-30, respectively. These membranes are hydrophobic in nature, and PE-30 is used in the manufacture of dry batteries. Composite polymeric membranes NTGS-1100 and NTGS-2100 having silicon as the active layer and polysulfone and polyimide as support layers, respectively, were obtained through the courtesy of M/s Nitto Denko Corporation, Kusatsu, Japan. These hydrophobic membranes were originally developed for gas-separation applications, NTGS-2100 is already in commercial use for hexane vapor recovery in the petroleum industry. The membranes were cut into circular discs (7.5 cm diameter and 32 cm^2 effective area) and fitted into the membrane cell.

Membrane apparatus. The flat-membrane test cell (Nitto Denko Corporation, Kusatsu, Japan) was operated in the batch mode. Experiments were conducted under a nitrogen atmosphere, and the operating pressure was maintained by adjusting the pressure regulator of the nitrogen cylinder. The membrane cell was placed on a magnetic stirrer, and agitation was provided by the magnetic spin bar fitted into the cell (Fig. 1). The membrane cell with the magnetic stirrer was kept in a thermostatically controlled incubator. The cell was charged with a fixed quantity of crude vegetable oil. The permeated oil was collected through a port beneath the membrane support; hourly, the flux was recorded by a personal computer (PC-286L; Epson, Shiojiri, Japan), that was interfaced with an electronic balance (FX-300; A & D Limited, Tokyo, Japan).

Batch experiments. Experiments were conducted with microfiltration membranes and crude soybean and rapeseed oils. The pressure, temperature, and rotation of the magnetic spin bar were maintained at 0.3–0.5 MPa, 40°C, and 800 rpm, respectively. The initial feed was 100 g of crude oil, and the experiment was stopped when the permeate collection was approximately 50 g. Batch experiments with polymeric composite membranes were conducted with crude soybean oil at the same operating conditions and at 3 MPa.

Ethanol conditioning and membrane cleaning. The NTGS-2100 membrane was conditioned in ethanol to check membrane stability and to evaluate ethanol as a cleaning agent. The membrane was soaked in ethanol for 22 h, the safest and mildest solvent, before being fitted into the membrane cell. The performance of the membrane was evaluated after 4–6 permeate collections. Studies were also conducted with membranes that were cleaned with ethanol without conditioning. The membrane was cleaned by dipping in ethanol for 1 min, and was removed immediately; the surface was gently wiped with a soft tissue paper. Cleaning was done randomly after collecting 2–6 permeates from the test cell. The membrane surface was smeared with refined oil immediately after the ethanol treatment to avoid surface drying.

Long-term experiments. Long-term experiments were conducted with NTGS-2100 at 2 and 3 MPa and with NTGS-1100 at 3 MPa. The temperature was maintained at 40°C, and rotation of the spin bar was controlled at 800 rpm. During experimentation, samples were collected when approximately 50 g of oil had permeated through the membrane, the cell was depressurized, and fresh feed was added to the retentate to make the oil quantity up to 100 g before the unit was restarted. There was some loss of retentate during depressurization in the form of foam; this was compensated for by the addition of more crude oil. A reasonably good mass balance could be obtained. The number of operating days and the total number of permeates collected were different in all three runs due to differences in permeate flux. NTGS-2100 at 2 MPa was operated for a maximum time duration of 97 d. NTGS-1100 had a higher flux, and the maximum number of permeates (53 permeates) was collected over a period of nearly 48 d.

Analyses. Phosphorus contents of the samples were measured by the standard molybdenum blue method (Ca 12-55) of AOCS (12). Absorbance values at 650 nm were recorded by a spectrophotometer (Hitachi U-1100, Hitachi, Japan). Chemicals used were of analytical grade and procured from

TABLE 1
Phospholipid Content of Crude, Membrane-Processed, and Conventionally-Processed Soybean and Rapeseed Oil Samples

	Phospholipid content (mg/kg)		Phospholipid reduction (%)	
Sample type	Soybean	Rapeseed	Soybean	Rapeseed
Crude	5370	6060	—	—
Membrane process				
Permeate of NTGS-1100	18	213	99.7	96.5
Permeate of NTGS-2100	27	9	99.5	99.9
Conventional process				
Degummed	4140	4200	22.9	30.7
Deacidified	72	—	98.7	—
Bleached	27	0	99.5	100.0
Deodorized	15	0	99.7	100.0

reputable companies in Japan.

Performance parameters. The performance of the membrane process was expressed in terms of permeate flux, percent rejection of phospholipids, and phospholipid content in the permeates. Phosphatide or phospholipid equivalent was calculated by multiplying the phosphorus content by a factor of 30 (12). Mass balances were calculated from the phosphatide values and the measured weights of permeates, retentates, and feed material added. The percent observed rejection of phospholipids for each permeate collected was determined, by assuming that it was constant during each experimental batch, from the following equation (13):

$$R_o = \frac{100[\ln(C_{R_f}/C_{R_i})]}{\ln(W_i/W_f)} \quad [1]$$

where C_{R_i} and C_{R_f} are the initial and final phospholipid contents in the retentates (mg/kg-oil), and W_i and W_f are the initial and final retentate weights (kg-oil), respectively.

RESULTS AND DISCUSSION

Batch experiments with microfiltration membranes. PE-30 gave the maximal normalized permeate flux of 12.6 kg/(m^2 • h • MPa). PE-10 permeated only about 10 g over a period of nearly 3 d. The void volumes of PE-10, PE-20, and PE-30 were estimated by measuring the weight gained after soaking the membranes in pure soybean oil for 4 h, and the values had a ratio of 1.0:2.0:2.6. The normalized flux of PE-10 was much lower than expected, possibly due to a more tortuous pore structure with blind passages. The phospholipid rejection by PE-10, PE-20, and PE-30 membranes were 12.1, 9.8, and 8.7%, respectively. The low rejection of phospholipids indicated that most of the reverse micelles formed in the system were smaller than the pore size, 0.01–0.03 μm, of the membranes. In view of the unacceptably low rejection, it was decided to conduct further experiments with new-generation composite polymeric membranes.

Batch experiments with polymeric composite membranes. Phospholipid contents of crude, membrane-processed, and conventionally processed oils are given in Table 1. In membrane degumming of soybean oil, the phospholipid content was reduced by 99.7% and 99.5% in the permeates of NTGS-1100 and NTGS-2100, respectively. In the conventional process, water degumming reduced the phospholipid content by 22.9%, mostly due to hydratable phospholipids, and the maximum reduction in phospholipid content occurred during the deacidification and bleaching steps. In membrane processing, the near complete removal of phospholipids in a single step indicated that the membranes rejected not only hydratable but also nonhydratable phospholipids. The reduction in phospholipid content in the membrane process was much higher than in the water-degumming process. For rapeseed oil, NTGS-2100 showed better selectivity, possibly attributable to the nature of the membrane and its composition.

Effect of ethanol treatment on membrane performance. The performance of NTGS-2100 with and without ethanol treatment on the permeate flux, the percent of phospholipid rejection, and the phospholipid content in permeates is presented in Table 2. Membrane conditioning in ethanol improved the permeate flux without significantly affecting the rejection characteristics, compared to the unconditioned membrane (membranes 2 and 1). The use of ethanol as a cleaning agent increased the permeate flux, but phospholipid rejection decreased significantly. Membranes (3 and 4) failed immediately after the second cleaning, irrespective of the duration of operation, demonstrating that the life of the membrane depends on the cleaning method and number of clean-

TABLE 2
Effect of Ethanol Treatment on Membrane (NTGS-2100) Performance[a]

Membrane number	Treatment		Number of permeates	Average permeate flux [kg/(m^2 • h)]	Average phospholipid content of permeates (mg/kg)	Rejection of phospholipids (%)
	Conditioning	Number of cleanings				
1	No	trace	6	0.21	327	99.4
2	Yes	trace	4	0.36	633	98.4
3	No	trace	4	0.21	252	99.4
		First	2	0.31	1548	93.7
		Second	1	0.76	9150	51.1
4	No	trace	6	0.21	327	99.4
		First	6	0.24	474	98.0
		Second	1	0.64	5700	71.8

[a]Phospholipid content of crude soybean oil is 15,960 mg/kg.

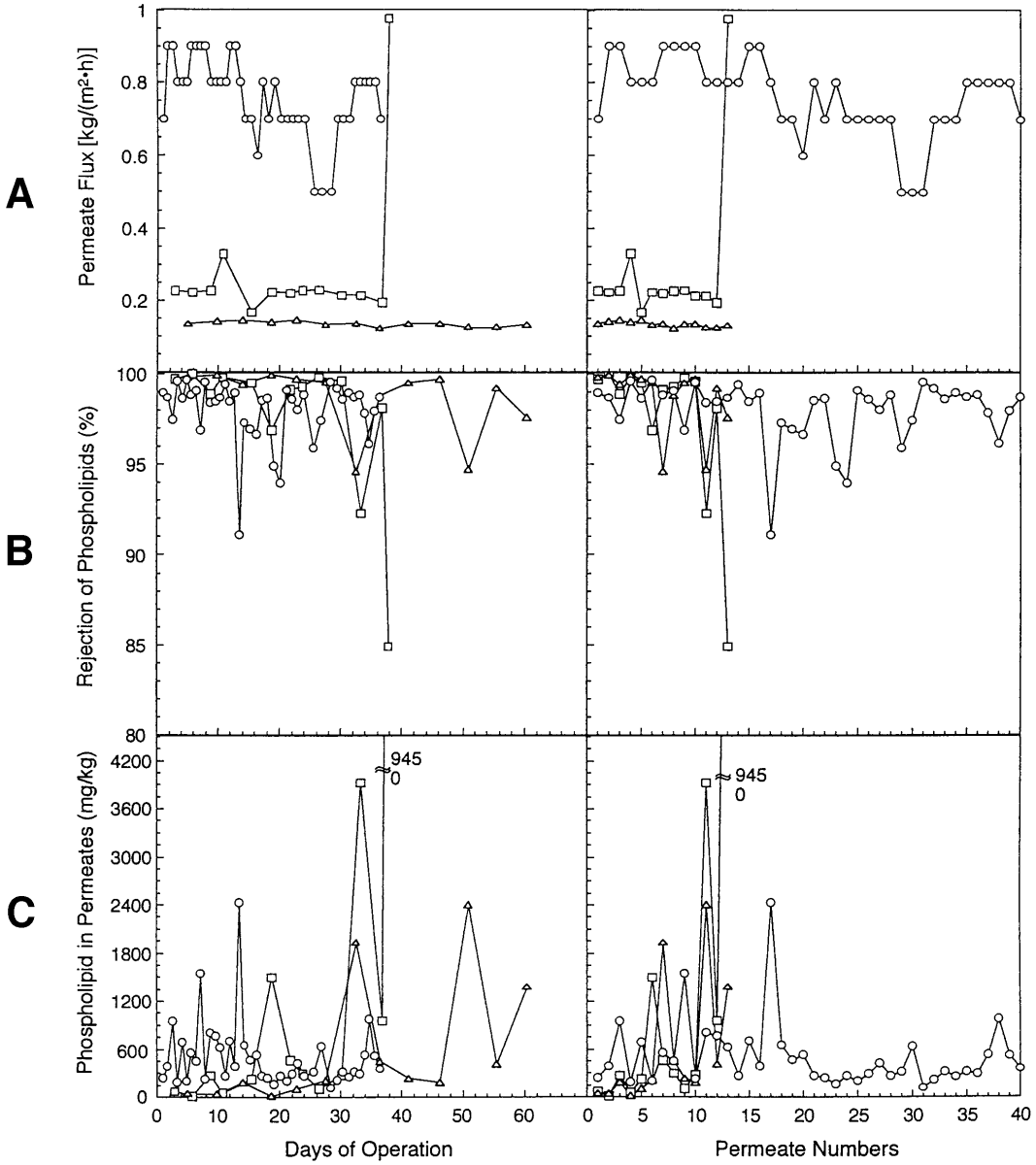

FIG. 2. (A) Changes in permeate flux (top); (B) phospholipids rejection; (C) phospholipid content in permeates during membrane degumming process (□, NTGS-2100, 3 MPa; △, NTGS-2100, 2 MPa; and ○, NTGS-1100, 3 MPa).

ings rather than the quantity of permeate collected or duration of the operation. This physical damage may be attributed to the combined effect of high operating pressure and repeated exposure to ethanol. Hence, long-term experiments were conducted with membranes devoid of conditioning and cleaning with ethanol.

Long-term experiments. Figure 2 shows the performance of NTGS-2100 and NTGS-1100 membranes on permeate flux, percent rejection of phospholipids, and phospholipid content in the permeates vs. days of operation as well as quantity of permeate collected. The experiments with NTGS-2100 at 3 and 2 MPa and with NTGS-1100 at 3 MPa were continued for up to 38, 97, and 48 d, during which 13, 20, and 53 permeates were collected, respectively. Not all data are presented in Figure 2.

The NTGS-2100 membrane at 3 MPa gave an average permeate flux of 0.22 kg/(m^2 • h) with minor fluctuations (Fig. 2A). This experiment could not be continued beyond 38 d due to membrane failure, which resulted in a rapid increase in the permeate flux. Visual inspection of the membrane revealed that a small portion of the active layer had peeled away from the support layer. Hence, the second experiment was conducted with NTGS-2100 at a lower operating pressure of 2 MPa, reducing the flux to 0.13 kg/(m^2 • h) but remained stable until the end of the experimental period. At 3 MPa operating pressure, the NTGS-1100 membrane gave an average flux of 0.75 kg/(m^2 • h), with some fluctuations, about three times higher than the average flux of NTGS-2100 at the same

operating pressure.

The NTGS-1100 and NTGS-2100 membranes performed well in rejecting phospholipids. The rejection was above 93% in most permeates (except in a few experiments), and the majority rejected more than 96% (Fig. 2B) in spite of the increase in the phospholipid content of the retentate after each collected permeate. The performance of NTGS-1100 was more stable in rejecting phospholipids throughout the experimental period. The phospholipid content was below 900 mg/kg in most permeates, except for a few, in all three experiments (Fig. 2C). The phospholipid contents of the last permeate (number 53) and its retentate of NTGS-1100 were 57 and 66,900 mg/kg, respectively.

From present findings and the literature, it is clear that the degumming performance of the composite polymeric membranes (NTGS-1100 and NTGS-2100) was much better than the water-degumming process and compared favorably with the super-degumming process. Besides, the long-term experiments indicated that these membranes had a reasonably long life at appropriate operating pressures. However, the permeate flux must be improved significantly for industrial adoption.

Phospholipids are triglycerides that contain phosphoric acid as a mono- or di-ester (11). These surfactants have both hydrophobic and hydrophilic groups. The average molecular weight of phospholipids is around 700 Da, and that of neutral triglycerides is 900 Da. Despite this, membranes rejected phospholipids while triglycerides permeated, this is probably the result of the formation of reverse micelles. The hydrophilic polar heads are inward in the reverse micelles and interact with other polar compounds. The larger complex formed can be easily separated by membranes, and hence, use of polymeric membranes seems to be an alternate process for the conventional degumming method. However, successful separation depends upon several factors, such as temperature, critical surfactant concentration, pH, membrane composition and pore size, and the extent of interaction between the surfactant reverse micelle and other impurities. Studies are being continued to produce a viable and more comprehensive membrane refining process for vegetable oils, for industry adoption.

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