Removal of phospholipids from crude edible oil by PVDF membrane

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ABSTRACT

Removal of phospholipid is the first step in the process of filtering crude edible oil. Membrane separation has been proposed often as an alternative to the conventional process. Until now, the instability of polymeric membrane in organic solvent was the main issue but in this work, we synthesized PVDF membrane of different composition to evaluate their flux and rejection properties. Degumming experiment of crude peanut oil miscella was performed using two PVDF samples. Among them, a fresh sample (M-3) gave higher flux of 47.5 LMH and rejection of 94% with increasing stability.

Keywords: *Phospholipid, Crude peanut oil, PVDF membrane, Characterization, Permeate flux, Rejection.*

1. INTRODUCTION

In rapid globalization and growth of world population, scarcity of water has become a critical issue which needs more attention to overcome the existing water crisis.[1] Crude edible oil contain mainly triacylglycerols (or triglyceride) and some slight components such as phospholipids, free fatty acids, sterols, colouring pigments, proteins and oxidation products which harmfully affect the final product and the processing efficiency.[2] These impurities are removed at various steps in conventional chemical refining namely degumming, neutralization, washing, drying, bleaching, filtration and deodorization.[3] The process has remained unchanged in recent decades even though it presents numerous drawbacks, such as high energy requirements, loss of neutral oil, the need of large amount of water and chemicals, loss of nutrients and disposal of highly polluted effluents. The application of membranes in edible oil refining has been investigated for their potential for energy savings as well as their potential for improvement in oil quality, allowing combination of degumming and bleaching into a single step, thus reducing energy requirements and making

the use of chemicals unnecessary.[4] Membrane technology is the most cost-effective and less-energy intensive process among all the separation processes.[5] Owing to a vast scope of this separation technique and potential for improvement in oil quality, edible oil processing has become one of the prime areas of membrane application.[6] One of the key steps in oil refining process is to eliminate the impurities from crude edible oils especially the phosphatides or so-called gums. They are mainly present in all oils extracted from seeds. They have to be removed in the early refining stages for the reason: the phospholipids can act as emulsifying agents, leads to loss of neutral oil, and result in a low-grade finished product, and also responsible for deterioration during storage. There are two types of phospholipids available in the oil: hydratable phosphatides and nonhydratable phosphatides (NHP).[7] Degumming is first step in the oil refining for quality improvement by removal of gums, phospholipids, free fatty acids (FFA), waxes and coloured pigments from oil. At the same time the process is required to reduce oil losses, stop decolourization and oxidative degradation of oil. Phospholipids and triacylglycerols are difficult to be separated by molecular sieving separation process because of closeness of their molecular weighs which are in the range of 700-900Da.[8] However, phospholipids are surfactants, having both hydrophobic and hydrophilic groups, and forms reverse micelles in non-aqueous system such as oil/hexane miscella with an average MW of 20,000Da that enables their separation by using of appropriate membranes.[9] The membrane separation being a physical process does not include chemical changes of oil constituents thereby retaining micronutrients besides its cost-effectiveness and low-energy intensive process, which is advantageous over conventional chemical separation processes. Such membrane for degumming application generally exhibit Molecular-Weight-Cut-Off (MWCO) of about 20000 g/mol. Different types of polymeric substances can be used to prepare membranes like polyimide (PI), polysulfone (PS), polyacrylonitrile (PAN),

cellulose acetate, polyvinylidene fluoride (PVDF) etc. Degumming of crude edible oil using various membranes have been investigated by many researchers. Flat sheet membrane from polyethersulphone (PES), of 101.9 kDa (BASF, E-6010, Germany) was prepared by employing phase inversion process using N'N' Dimethylformamide (DMF) as a solvent to form 12% polymer solution. This membrane was tested for 25% soyabean oil/hexane miscella which gives 89% phospholipid rejection at decreasing permeate flux with time-tested in stirred dead-end test cell.[10] Another membrane made of Mavibran FP055A flat sheet (MWCO 55 kDa, 100 cm^2 surface area) and Mavibran SP015A flat sheet (MWCO 15 kDa, 100 cm^2 surface area) were tested for phospholipid removal from desolventized crude soybean and sunflower oil. Comparing both SP015A membrane had 70-77% retention of phospholipid.[11] Pagliero & Ocha[12] had performed the degumming experiment with two different membranes. One of them is commercially available UF membrane made of polyimide (PI), which is obtained from a worldwide membrane supplier (MPS-U20-S, Koch Membrane System Inc. Wilmington, MA). The other one is PVDF synthesized in their laboratory. The degumming experiment was performed with two different experimental setups, stirred dead-end cell and tangential flow UF cell at different temperature and velocity flow. The results show compare to PI, PVDF is better in selectivity, permeate flux and retention. In another report, two types of tubular polyethersulphone (with molecular weight cut off 4000 Da and 9000 Da) membranes were prepared for degumming of 30% sunflower oil /n-hexane miscella in a cross flow pilot plant. Both membranes gave rejection up to 95-97% although membrane prepared with MWCO-9000 Da polyethersulphone was given higher flux.[13] Another degumming experiment was carried out using 30% micsella of crude rice bran oil in the solvent following by commercially available flat sheet membranes, 50 kDa PVDF (Maua, Brazil), 75 kDa PVDF (Wiesbaden, Germany) and 5 kDa PES (Wiesbaden, Germany). Hexane is used for PVDF and anhydrous ethyl alcohol for PES as a solvent. The 75 kDa PVDF membrane displayed high average flux of 55.8 LMH because of large pore diameter with 82.3% phospholipid rejection. Whereas 5 kDa PES membrane showed 62% phospholipid rejection with an average flux of 49.5 LMH.[14] Comparing to all the membranes used for degumming experiment PVDF membrane allowed higher permeate fluxes and gave promising results regarding their stability in solvent and good amount of phospholipid rejection.

Preparation of PVDF membranes suitable for the degumming of edible oil is explored by casting of PVDF dope under optimum preparation condition by the phase inversion technique. The aim of the work is to study the effects of different parameters on membrane morphology and prepare the PVDF membrane with higher productivity throughputs (flux) and better separation selectivity (gums, phospholipids, waxes, pigments etc.). Different results were observed in the preparation of PVDF membranes with variations in types of PVDF and modifications relating changes in concentrations of polymer, the addition of pore-forming additives, casting procedures and post modifications of base membrane. Comparisons were made between the membranes in terms of flux and MWCO as well as characterization of membrane surface energy, hydrophobicity and microstructure morphology. The PVDF membrane with desired properties, which is stable in an organic solvent (n-hexane) for degumming application of edible oil processing, can be prepared conveniently by casting over a porous support

continuously driven by a motorized machine under optimum preparation conditions.

In the present work, PVDF hollow fiber membranes were prepared using different compositions, additives, and spinning parameters. These ultrafiltration membranes were conveniently spun from polymer solutions at room temperature. The membrane structure was varied in terms of their mechanical strength, membrane morphology with different pore sizes. The prepared PVDF hollow fiber membranes were used for processing crude peanut oil obtained from local market. The oil/hexane miscella was prepared with hexane (70%) and crude peanut oil (30%). These membranes were thoroughly characterized and explored for its potential in the removal of phospholipid.

2. EXPERIMENTAL

2.1 Materials

PVDF homopolymer (Mw, 570 - 600 kDa) with trade name Solef® 1015 was supplied from Solvay Advanced Polymer, USA. N-Methyl-2-pyrrolidinone (NMP) from Spectrochem Pvt. Ltd. and Ethylene Glycol (EG) from Himedia, India were purchased. Liq. NH$_3$ (25% solution) was obtained from Ranbaxy chemical Pvt. Ltd., India. Polyethylene oxide (PEO) of 100 kDa and 200 kDa molecular weight (Mw) were purchased from Sigma Aldrich, India. All chemicals were of analytical grade and used without any further treatment. Nitrogen (N$_2$, 99.9 %) gas cylinder was supplied from Parshav Chem. India.

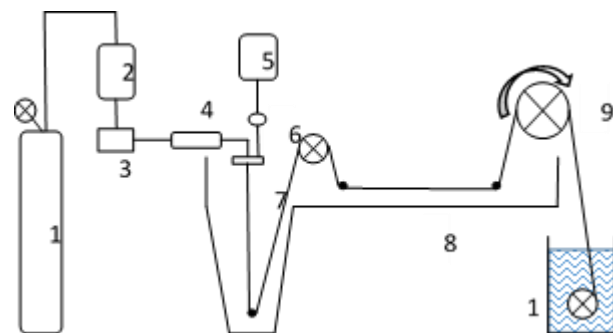### 2.2 Preparation of PVDF polymer dope solutions with additives

For the preparation of polymer dope solution, PVDF powder was dried in the oven at 80°C for 24h to remove its moisture before preparing the polymer dope solution. The desired amount of dried PVDF powder was dissolved in NMP solvent at 60°C temperature under continuous stirring using the axial propeller type mechanical stirrer at 1200 rpm until the homogeneous transparent solution was obtained. To study the effect of the additives on polymer performance, selective additives (EG and liq. NH$_3$) were mixed in the dope solution and keep stirring in order to get a homogeneous solution. The prepared dope solution was allowed to cool by standing at room temperature for overnight and to remove the trapped air bubbles from the dope solution. All the polymer compositions are summarized in Table 1.

Table 1. Compositions of prepared PVDF polymer dope solutions

Membranes	Polymer dope compositions (w/w %)			
	PVDF	NMP	EG	Liq. NH$_3$
M-1	13	79	8	-
M-2	14	78	8	-
M-3	15	75	10	-
M-4	14	76	-	10
M-5	17	83	-	-

2.2 Spinning of PVDF hollow fiber membranes

The aforementioned polymer dope solutions were extruded through double orifice spinneret under the N2 atmosphere to spun asymmetric PVDF hollow fiber membranes using the spinning unit as shown in Fig. 1 The spinning parameters to prepare hollow fiber membranes are described in Table 2. Pure water was used as an inner coagulant, which flowed through the inner nozzle of the spinneret and starts the coagulation of fiber from inner side prior to contact external coagulant. The bore fluid causes the phase inversion from inside followed by outside phase inversion in an external coagulation bath. The spun hollow fiber membranes were collected in a water reservoir with the continuous winding on the bobbin and were kept in water for 24 h for complete gelation. These membranes were washed several times with normal and hot water to remove residual solvent from the membranes.

Table 2. Spinning parameters used for the preparation of different PVDF hollow fiber membranes

| Spinning parameters	Hollow fiber membranes				
	M-1	M-2	M-3	M-4	M-5
Spinneret: (O.D./I.D) μm	1000/600	1000/600	1000/600	1000/600	1000/600
N_2 Pressure (kPa)	100	100	100	100	100
Extrusion rate (g/min)	5.3	6.7	6.2	6.8	5.8
Inner coagulant	Pure water	Pure water	Pure water	Pure water	Pure water
Bore Permeate flow rate (ml/min)	24	24	25	24	24
External coagulant	Pure water	Pure water	Pure water	Pure water	Pure water
Wind-up rate (m/min)	30	30	32	30	30
Coagulant temperature	25°C	25°C	25°C	25°C	25°C
Air gap	2.4	2.4	1	1	2.4

Figure 1. Schematic diagram of spinning unit: 1. Nitrogen Cylinder 2. Dope Solution Tank 3. Gear System 4. Prefilter 5. Bore fluid 6. Peristaltic pump 7.Spinneret 8. Coagulation bath 9. Winding bobbin 10. Collection tank

2.3 Fabrication of Ultrafiltration module

The ultrafiltration modules of 15-20 cm in length and 5 cm diameter containing 25-30 fibers were prepared by potting PVDF hollow fiber membranes inside the module using commercially available epoxy resin. Both ends of the module containing fibers were fixed with resin and only membranes bore area was kept open. These modules were tested for pure water flux and Molecular Weight Cut-off (MWCO) study operated from "into out" mode at positive pressure. The schematic of ultrafiltration module is shown in Fig. 2. The packing density of around 45%-60% was decided on the basis of the number of fibers inside the module. [16]
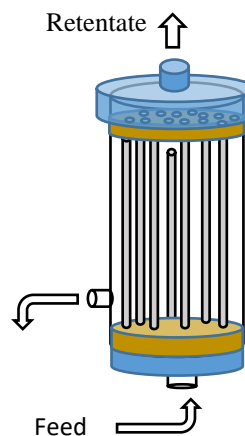
Figure 2. Schematic diagrams of ultrafiltration module design

$$Packing\ density = \left(\frac{Area\ of\ hollow\ fiber\ inner\ diameter}{Area\ of\ outer\ diameter\ of\ module}\right) \times Number\ of\ fibers \qquad (1)$$

2.4 Membrane characterization

The morphologies of the prepared membranes were examined using scanning electron microscope (Carl-Zeiss), model LEO 1430 VP at accelerating voltage of 20kV different magnifications. For sample preparation, hollow fiber membranes were fractured in liquid nitrogen and mounted on

stub then kept in a desiccator to keep moisture free. The gold coating was applied by sputter coater to make the sample electrical conductive. Membrane surface and cross-section images were recorded. The contact angle (water) measurements of the prepared membranes were carried out on DSA Kruss GmbH instrument at room temperature. The water droplet of 2µm was dropped from the microsyringe at 3 - 4 different locations of the membrane in order to calculate the contact angle. The tensile strength of the prepared membranes was measured using UTM (Universal tensile Machine) ZwickLine Z-2.5, Germany.

2.5 Pure water flux and MWCO study

The water flux of prepared hollow fiber membranes was measured in a cross-flow mode using ultrafiltration modules. The experiments were repeated at least three times to calculate the average water flux. MWCO (Molecular weight cut-off) of the membranes using high molecular weight PEO of 100 and 200 kDa were analyzed using gel permeation chromatography (GPC, Waters 2695 Module 2414 RI detector). MWCO is the molecular weight of the molecules that is 90% retained by the membrane. The concentration of the solutes in the feed (C_f) and permeate (C_p) were analyzed and the rejection (%R) of the solute was calculated using the following equation,

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (2)$$

## 2.6 Characteristics of the phospholipid

Phosphorous content of the feed and permeate were measured by using standard AOCS method Ca 12-55. This method determines phosphorous by making an ash of the oil sample in the presence of zinc oxide, followed by the UV-spectrophotometric measurement of phosphorous as a blue phosphomolybdic acid complex.

3. RESULT AND DISCUSSION

3.1 SEM study of PVDF hollow fiber membranes

The morphologies of the prepared PVDF hollow fiber membranes were studied using SEM analysis. As can be seen from SEM images M-1 have a highly porous structure with asymmetric morphology containing large finger-like macro voids it can be attributed to less polymer amount (13 wt. %) with EG additive (8 wt. %), which was used as a pore former and left the membrane with highly porous microstructure. M-2 membranes with slight higher polymer concentration, 14 wt. % containing similar EG concentration (8 wt. %) were examined and nearly similar microstructure was observed in the membranes. To get the porous microstructure with controlled membrane morphology, M-3 membranes (15 wt. %) with high EG concentration of 10 wt. % were prepared to have regular tear drop microstructure in the membrane. Polymer morphology with comparatively dense microstructure can be seen for M-4 membranes where the liq. NH_3 was used as an additive. EG and liq. NH_3 are the water soluble additives which dissolves in the nonsolvent coagulant water. Water as an internal and external coagulant diffuses quickly into the membrane structure and results in the asymmetric membrane morphology. Fiber wall of M-5 (17 wt. %) membranes without any additive consists teardrop microvoids at lumen side and regular finger like macrovoids

at outer side. Fig. 3. The physical properties of hollow fiber membranes are summarised in Table 4.
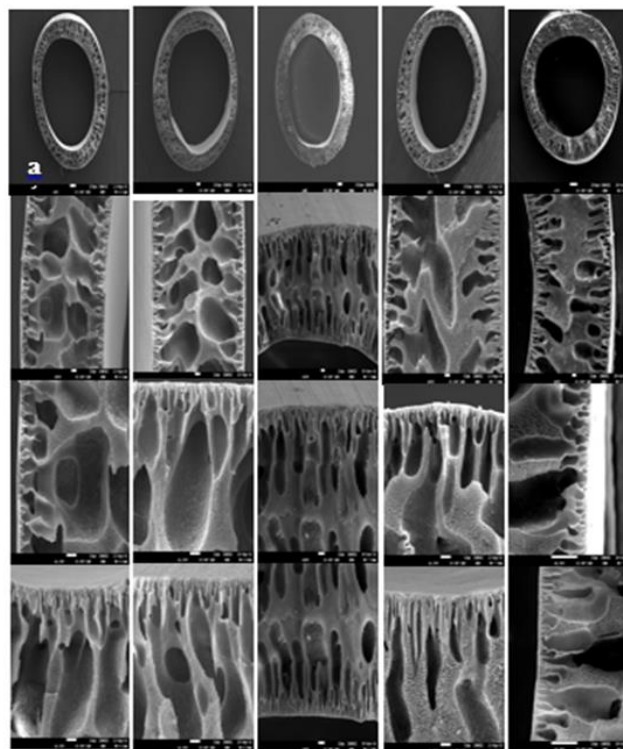
Figure 3: SEM images; full cross-sectional images, a(i)-e(i); magnified view of fiber wall, a(ii)-e(ii); highly magnified images of outer side, a(iii)-e(iii); and lumen side, a(iv)-e(iv) of M-1, M-2, M-3, M-4 and M-5 PVDF hollow fiber membranes respectively.

Table 4: Properties of spun PVDF hollow fiber membranes

Membrane characteristics	M-1	M-2	M-3	M-4	M-5
Outer Diameter(mm)	1.33	2.30	1.48	1.48	1.28
Inner Diameter (mm)	1.12	1.67	1.32	1.1	0.93

3.2 Tensile strength and hydrophobicity of the membranes

The tensile strength of membranes with different composition (i.e. M-1 to M-5) was evaluated using Universal Tensile Machine (UTM). The main aim of this test was to determine the strength of the fibers and the amount of deformation that could be expected after giving a certain load. The fibers were held between two jaws of the UTM and percentage elongation with the force at break (F_{Break}) in membranes were evaluated by applying load on the membranes. The F_{Break} is the maximum stress that the fibers can withstand. At least three specimens were evaluated for each fiber testing. Standard force sustains by M-5 was maximum, while the Strain percentage of M-3 was more compare to other three membranes M-1, M-2, and M-4 as shown in Fig. 4. The tensile strength of membranes extensively affects the performance of the membranes.
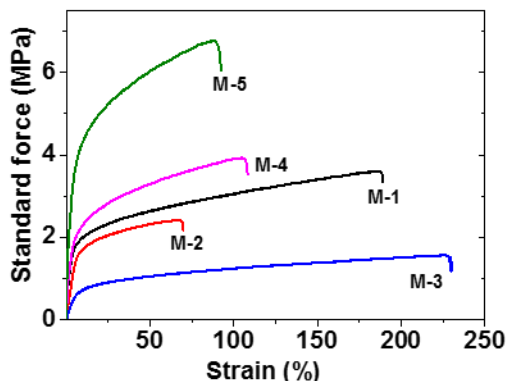
Figure 4: Tensile strength measurements of prepared membranes

The water contact angle of hollow fiber membranes of different compositions was estimated as results are shown in Table 5. The contact angle of the membrane also dependent on spinning conditions. [18]

Table 5: Tensile strength and water contact angle measurement

Membranes	Tensile strength		Contact angle (°)
	F_{Break} (Mpa)	dL at Break (%)	
M-1	3.34	190.1	73.2
M-2	2.17	70.3	77.9
M-3	1.31	32.5	78.7
M-4	3.52	106.2	80.7
M-5	6.05	93.4	82.9

In general lower contact angle signifies more hydrophilic nature. Nearly similar contact angle values were observed for M-1 to M-3 membranes due to the addition of EG in all three polymer dope solutions. On addition of liq. NH_3 to the dope solution, it resulted localized micro phase separation with micro cluster formation inside the PVDF dope solution. During phase inversion, these clusters grown completely into spherical particles on the membrane surface. [17] Liq. NH_3 undergoes a dehydrofluorination reaction between hydrogen and fluoride atoms present in the PVDF polymer chain. This crosslinking of the polymer chains is responsible for high contact angle of 80.70 for M-4 membrane. In case of M-5 membranes, higher contact values were observed among other membranes which were due to their high polymer concentration without the addition of the additives.

3.3 Pure water permeability and rejection performance of the membranes

The water flux of the prepared hollow fiber membranes was measured in a cross-flow mode. The feed water was supplied from bore side of the membrane using "in to out" mode and permeate was collected from the outside of the membrane. The water flux values were taken after the equilibrium was

achieved during the experiments. Different water flux and rejection profiles were observed for the membranes prepared from different compositions. Membrane M-1 had shown high flux of 157 LMH/bar with the low rejection of 45 and 55% for PEO 100 kDa and 200 kDa M_w respectively. In case of M-5 membrane with no additive, exhibited low flux of 25 LMH/bar with 100% rejection of PEO (100 kDa and 200 kDa, M_w). Optimum water flux of 80.45 LMH/bar with a complete rejection of PEO was observed for M-3 membrane. These membranes i.e. M-3 with excellent flux and rejection properties were used for the preparation of MBR module. The flux and rejection data for all the membranes are shown in Table 6. The increment in the volume flux was observed at the vacuum pressure of 100, 150 and 200 mmHg.

Table 6: Water flux and rejection performance of the membranes

Membranes	Flux (LMH/bar)	Rejection (%)	
		100 kDa	200 kDa
M-1	157	45	55
M-2	73	73	80
M-3	80	100	100
M-4	40	82	90
M-5	25	100	100

3.4 Phospholipid removal using hollow fiber module system

The hexane permeability of membrane M-2 is compared with run-time in the range of 50-350 minutes at room temperature and 5 bar constant operating pressure. From the Figure 5, it showed that M-3 membrane exhibited larger hexane flux than that of M-2 at the same operating condition. The effect of permeate on pure hexane flux from M-2 is quite minimum. At the beginning, the hexane flux was about 47.5 LMH that constantly declining to 40 LMH with run time up to 200 min, beyond which the hexane flux was constant with run time. The initial hexane flux decline for the M-3 was about 10%. In case of the M-2 membrane, the initial hexane flux was 16 LMH and the % hexane flux decline was almost two-fold as compared to that of the M-3 sample.
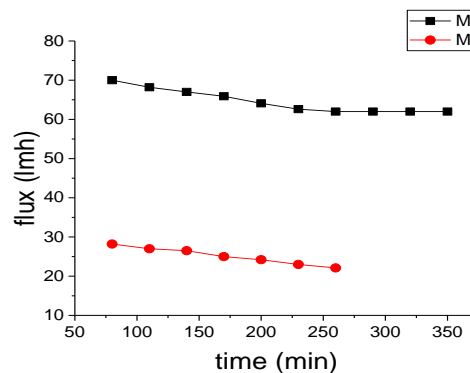

Fig

Fig.5. Comparison of the hexane permeability of two membranes M-3 and M-2 with run time at 5 bar operating pressure

The above M-3 membrane variants were examined in degumming of the miscella with 70% hexane with the objective of improving phospholipid removal, miscella flux and membrane stability in hexane. Figure 5 shows a significant change in the initial flux and flux decline for the membranes although all the membranes exhibited consistent phospholipid rejection 90~95% in all the runs. The M-3 membrane sample showed higher flux as compared to other membranes under all the experimental conditions. All two membrane shows flux decline at the beginning of the permeation process and after that, permeate flux remained almost constant for the period. The M-2 showed the lowest flux and highest flux decline 64%. The initial flux of 15 LMH exhibited by the M-3 was the highest among all the tested samples. The M-3 exhibited initial flux decline of about 20% which was the lowest and maximum phospholipid rejection of ~95% among all the samples.

4. CONCLUSION

Hollow fiber system has the potential for the removal of phospholipid. In this work, we have presented preparation and characterization of highly porous hollow fiber membranes spun from lower polymer concentration of 13 to 17 PVDF with or without pore former EG additives the optimally prepared hollow fiber MBR system exhibited excellent phospholipid reduction from crude peanut oil/hexane miscella. It could be a single–step pre-treatment process for physical refining and a better alternate process for conventional degumming in the chemical refining process, which is being widely practiced. The further process can be done by changing oil concentration and pressure conditions.

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