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Research paper

Screening of polymeric membranes for membrane assisted deacidification of sardine oil

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Abstract

The diversification in fish oil use and the need for softer processing demand new oil refining processes. In considering the advantages of membrane technology, three different membranes (polyamide (PA), polytetrafluoroethylene (PTFE) and polyethersulfone (PES)) were used in this particular study. Preliminary results in the separation of free fatty acids (FFA) from glycerides of sardine oil/ethanol mixtures using a single dead end microfiltration mode have been reported here. The influence of experimental factors like pressure and oil/ethanol ratios (w/v) on the permeate flux and the reduction of FFA (%) in the permeate was studied. PTFE membrane showed promising results in terms of residual FFA in permeate (%), % oil loss (15.12%, 5.45%) as compared to PA (20.50%, 6.66%) and PES membranes (20.60%, 8.92%). PA membrane showed a higher flux of 4.4 L/m^2/h, followed by PTFE 3.34 L/m^2/h and PES, 1.19 L/m^2/h at 3.5 bar trans-membrane pressure. These results showed that using PTFE membrane could be an ideal strategy for the membrane assisted deacidification of sardine oil using solvents.

Keywords: Deacidification; Ethanol; Flux; Free fatty acids; Membranes; Polytetrafluoroethylene; Sardine oil

1. Introduction

Membrane separations have been given much importance in the recent years due to ease of handling and the possibility of operations at milder conditions. The attraction posed by the membrane technology has led to their applications in water desalination, gas separation process and applications in food and pharmaceutical industries [1]. Membranes are a good alternative for all separation processes involving chemicals. Since membranes have been widely used in degumming stage, efforts were taken to exploit this application for deacidification step too. Several researchers have tried deacidification of oil by membranes with or without solvents. Many researchers have combined membrane technology and solvent extraction. Reports from Krishna Kumar and Bhowmick [2] and Raman, Cheryan, and Rajagopalan [3] emphasized on the removal of FFA from model oils. Mixtures of triglycerides and FFA with alcohol in the presence of both cellulosic and non-cellulosic type membranes were reported by Krishna Kumar and Bhowmick [2]. Processing of groundnut oil in the presence of alcohol and polyamide membrane led to the permeate having FFA of 86.8% when compared to the feed of 61.7% FFA concentration [4]. Hence, membrane technology delivers many advantages over the conventional processes, such as low energy consumption, operation at ambient temperature, no addition of chemicals, and maintenance of all the essential components in the oil. Edible processing of oil has become an important area in the field of membrane application due to the huge scope of energy savings and improvement in the quality of the oil.

Since many of the stated reports on solvent extraction and membrane assisted solvent extraction were focused on vegetable oils, a need to extend these methods for fish oils turns out to be a vital step in the field of refining. Among the different membranes, polymeric membranes have been given much importance due to their ease of fabrication, diverse properties and cost [5]. Due to the increasing interest in the membrane process of oil and fat industry, several studies on their application in degumming, deacidification, solvent recovery and color reduction have been performed [6]. Marine oils are considered to have an effective role in human health and nutrition due to

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the presence of n-3 polyunsaturated fatty acids (n-3 PUFA) [7]. Hence, replacing vegetable oils with fish oils has been given increasing significance. However, crude fish oil contains many impurities like phospholipids, free fatty acids, metal ions, pigments and oxidation products [8] that reduce oil quality. Therefore, in order to meet the safety standard refining treatments have to be employed.

The various stages in edible oil refining and the different methods under each stage have been critically reviewed by Vaisali et al. [8]. Of all the stages, removal of free fatty acids (FFA) is a crucial step due to the role of FFA in further oxidation. However, increased loss of neutral oil has been documented in the conventional alkali neutralization process [9], leading to the search of novel processes for effective deacidification in fish oil.

The current study focuses on such softer processing of sardine oil, involving the application of membrane separation, assisted by solvent extraction of FFA from sardine oil. Characterization of membrane process was done by determining the flux of oil/ethanol mixture, their ability to retain the membrane properties at increasing pressure. In order to gain maximum efficiency of deacidification, different types of microporous polymeric membranes were tested for their ability to separate FFA from oil/solvent mixture and also the separation of solvent from oil/solvent mixture. The lack of literature on the refining of sardine oil without the loss of its nutritional properties provides a scope for the current work, thus providing a novel approach to the problems in conventional deacidification.

2. Materials and methods

2.1. Materials

Crude sardine oil was purchased from a local seafood industry, Mukka, Mangalore. All chemicals and reagents were purchased from Merck, India, and were of analytical grade. Microporous polyamide membranes (0.45 μm) were purchased from Cole-Palmer, India. Polytetrafluoroethylene (PTFE) membranes (0.45 μm) were purchased from Axivia, India, and microporous polyethersulfone membranes (0.45 μm) were purchased from Sterlitech, USA. All membranes were in the form of discs of 10 cm diameter.

2.2. Methods

The crude sardine oil was subjected to degumming using 5% orthophosphoric acid and centrifuged at 5000 rpm for 20 min. The supernatant of the centrifuged oil (degummed oil) was further subjected to membrane deacidification. Membrane assisted solvent extraction was performed in the presence of hydrophobic membrane like polytetrafluoroethylene (PTFE), of pore size of 0.45 μm, polyamide membranes (0.45 μm) and microporous polyethersulfone membranes (0.45 μm) under various pressures (0.5 bar, 1 bar, 2 bar, 3 bar, 3.5 bar). The membrane unit of 10 cm diameter with a working volume of 500 mL which worked at a pressure range of 0.5 bar to 3.5 bar operated in the batch mode was employed for the present work (Fig. 1). The mixture in the membrane unit was continuously stirred using a magnetic stirrer. The degummed oil was stirred

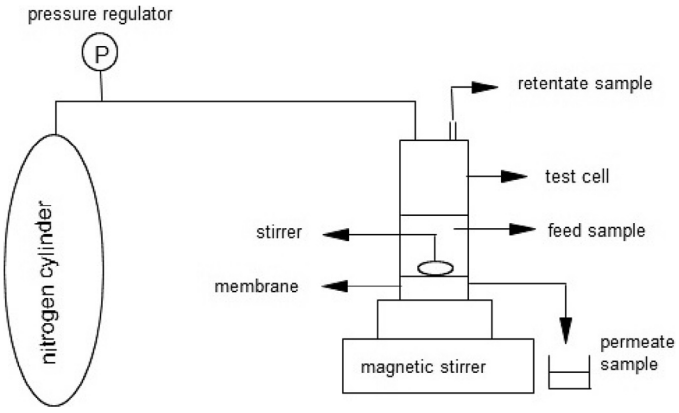

Fig. 1. Schematic representation of experimental test cell.

with ethanol for 1 h and the mixture was then subjected to separation. The permeate obtained was solvent free oil with the rejection of FFA and solvent. Further, the permeates were analyzed for FFA content. The indicators like FFA rejection in a membrane and flux were calculated as follows.

The FFA content was analyzed by determining the acid value as described in (AOCS) [10].

$$\%\ FFA\,(as\ oleic\ acid) = Acid\ value/1.99 \tag{1}$$

The membrane flux was calculated by the following equation.

$$Flux = Permeate\ quantity\,(L)/\left(area\ of\ \ filtration\,(m^2)\times Time\ of\ \ filtration\,(h)\right) \tag{2}$$

3. Results and discussion

The crude oil was tested for its properties and it was found to contain considerable amounts of FFA (30.22%) as indicated in Table 1. High concentrations of FFA in the oil are known to cause a rapid oxidation of the oil, which compels the requirement of its removal by deacidification. Hence, deacidification with three different polymeric membranes was tailor made with the purpose of removing FFA while improving the flux through the membrane.

The flux of sardine oil/ethanol mixture was studied for three membranes viz., PA, PES and PTFE. A very rapid reduction in the flux was observed for PA membrane and very low flux was seen through PES membranes (Fig. 2). The contribution to the decline in flux could be attributed to changes in the membrane structure [11]. As can be seen from Table 1, PA and PES membranes exhibit hydrophilic nature as compared to PTFE membranes, which is evident from the fact that the deacidified oil alone (hydrophobic in nature) is obtained as the retentate. The movement of the polar FFA molecules across the membranes might have caused the membranes to swell and become thicker plummeting the permeation rates [12]. However, in case of PTFE membrane, the flux was almost constant without any significant decline. The reason behind this could be the hydrophobic nature of the membrane, which is similar to the nature of the oil. Hence, there is no change in the membrane structure of PTFE when the oil alone permeates across the membranes.

Table 1
Characterization of the sardine oil after membrane assisted deacidification.

Parameters analyzed	Polyamide		Polyethersulfone		Polytetrafluoroethylene	
	Control*	Test[a]*	Control	Test[b]*	Control	Test[c]*
Acid value	60.15	40.8	60.15	41	60.15	30.1
% FFA (in terms of oleic acid)	30.22	20.50	30.22	20.60	30.22	15.12
% Oil loss	NA	8.20	NA	7.56	NA	1.45
Amount of solvent	NIL	6.66	NIL	8.92	NIL	0.53

* Control – plain degummed oil passed through the membrane; Test[a]*– deacidified oil as retentate; Test[b]*– deacidified oil as retentate; Test[c]* – deacidified oil as permeate.

By varying the pressure and oil/ethanol ratio, the membrane permeate flux of sardine oil/ethanol mixture was studied. Figs. 3 and 4 represent the effect of pressure and oil/solvent ratio on flux respectively. From Fig. 3, it is evident that PA showed the maximum flux at all pressures followed by PTFE and PES membranes. This could be because PA is a hydrophilic aromatic membrane which facilitates the easy movement of the oil/ethanol mixture in the ratio 1:2 due to the polar nature of ethanol. Also, in this ratio the oil micelles are probably smaller promoting easy permeation through the membrane. The increase in trans-membrane pressure increased the flux due to the higher driving force, according to Darcy's law [13]. Also, the increase in the permeation rate in all the membranes with increase in pressure indicates no compaction of membrane at this pressure range [11].

A negative effect on the flux was observed when the percentage of oil in the mixture increased from 20 to 80% (Fig. 4) at a high pressure of 3.5 bar. A drastic reduction in the flux across PA was seen with the increase in the oil concentration in the mixture. At low percentages of oil, the ethanol flux was higher, providing an efficient separation of ethanol and oil. However, with an increase in the oil concentration in the mixture, the hydrophobicity of the mixture increases, leading to fouling on the membranes with oil which leads to an improper separation of oil/ethanol mixture. On the other hand, PES and PTFE showed a steady decrease in the flux of the mixture. The reduction in the flux for all three membranes with the increase in oil concentration at high transmembrane pressures of 3.5 bar may be attributed to the compaction of the oil particles forming a layer on the membranes causing the reduction in the membrane pore size [13]. The increase in the percentage of oil in the mixture causes an increase in the viscosity. Viscosity affects the convective flow inversely, which is perhaps the reason for the decline in the flux across the three membranes with the increase in the oil concentration. A similar trend was observed by Koike et al. [14] while studying the performance of various polymeric membranes for sunflower oil mixture with solvents like ethanol and hexane.

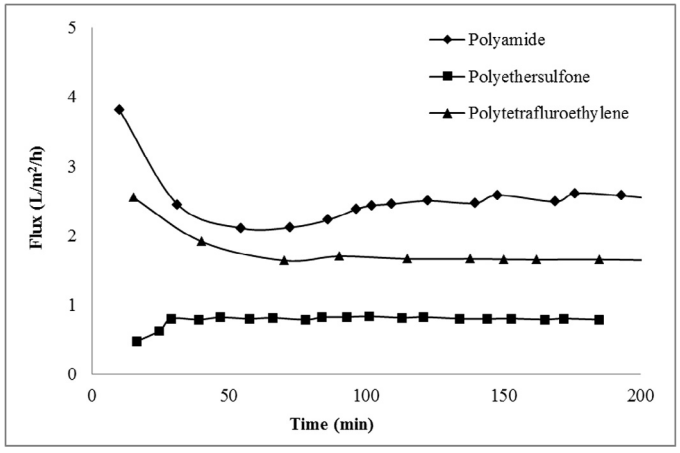

Fig. 2. Feed flux of sardine oil/ethanol mixture (1:2) at 3.5 bar and 200 rpm with a filtration area of 0.00785 m^2.

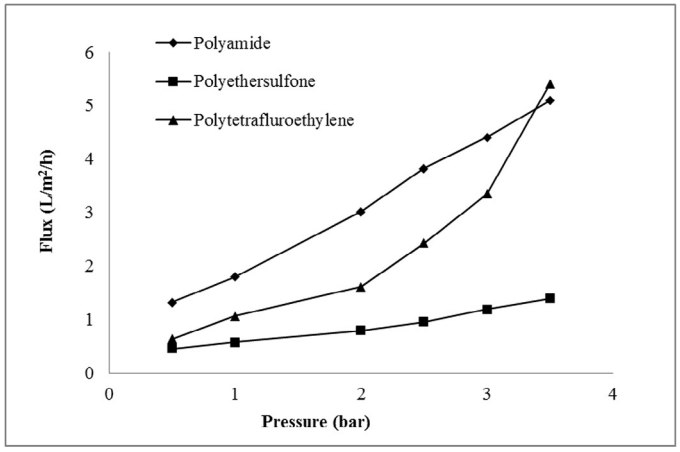

Fig. 3. Effect of pressure on the flux of oil/ethanol (1:2) mixture at 3.5 bar.

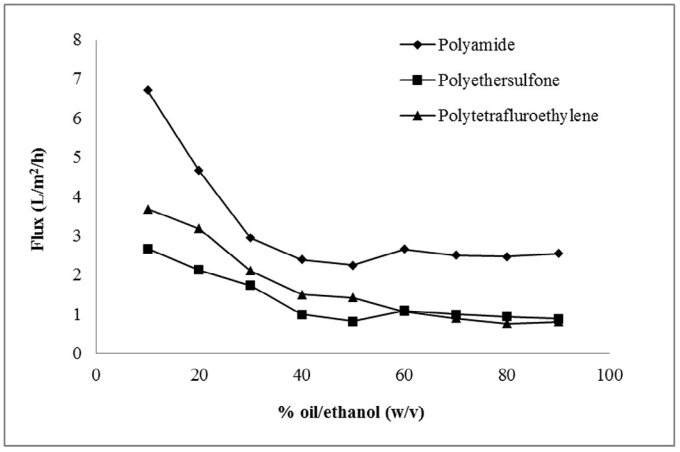

Fig. 4. Effect of oil/ethanol ratio on the flux of oil/ethanol mixture at 3.5 bar.

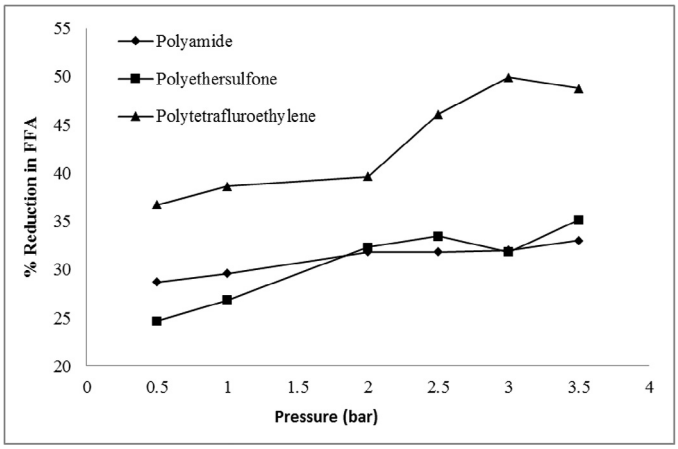

Fig. 5. Effect of pressure on the reduction of FFA from oil/ethanol (1:2) mixture.

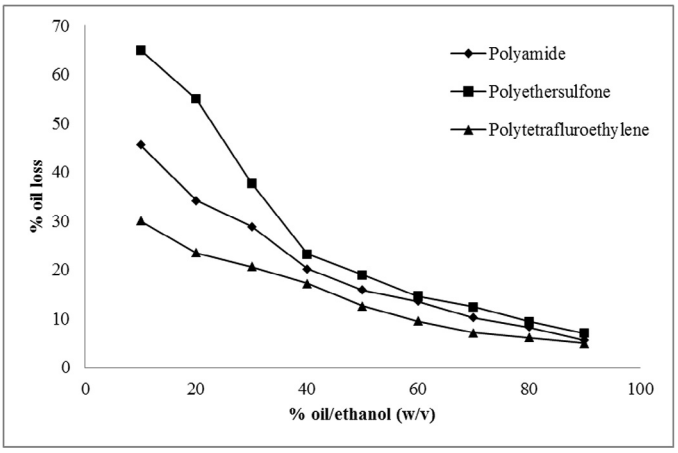

Fig. 6. Effect of oil concentration in the oil/ethanol mixture on the percentage oil loss. Experiments were conducted at a pressure of 3.5 bar and 200 rpm.

In case of the effect of pressure on FFA reduction with PA membrane, the increase in pressure did not affect the reduction of FFA from the mixture. In the reduction of the FFA from the mixture (Fig. 5) which is due to the improper separation of oil and ethanol phases. However, in case of PES and PTFE membranes, increasing the pressure from 0.5 to 3.5 bar increased the FFA reduction from 24.6 to 33% and from 36.7 to 49% respectively (Fig. 5). This was due to the resistance of the membrane for FFA which is known for the plasticizing effect on polymers [12]. This phenomenon could be explained by the hindered transport of FFA molecules in a mixture containing larger triglyceride molecules which is attributed to the nature of the membrane [15]. The ratio of oil/ethanol mixture was optimized by using conventional solvent extraction (data not shown) and 1:2 of oil/ethanol ratio was found to be optimum for maximum reduction of FFA. However, the percentage of oil loss has to be determined with respect to membrane experiments in order to find the significance of the membrane assisted deacidification of sardine oil at industrial level. Hence, the effect of oil concentration in the mixture on oil loss was determined to study the industrial relevance of current technology.

The percentage of oil loss was found to be highest for PES, regardless of the oil concentration in the mixture (Fig. 6), followed by PA. However, PTFE membranes showed the least percentage of oil loss from 30% to 10% at all oil concentrations from 20% to 80% (w/v) (Fig. 6). This is because of the hydrophobic nature of PTFE, which results in the complete separation of oil and ethanol from oil/ethanol micelle mixture at 3.5 bar. This is very similar to the results obtained by Rao et al. [16], when coconut oil was deacidified using polymeric membranes.

PA showed the highest flux of 4.4 L/m^2/h, followed by PTFE 3.34 L/m^2/h and PES 1.19 L/m^2/h at 3.5 bar. The chemical characterization of sardine oil before and after the membrane process was analyzed and reported in Table 1. It was evident that PTFE membrane was effective in reducing FFA, lowered the oil loss as well as the amount of solvent in the oil. The reduction of the solvent content in the oil by PTFE was due to the high selectivity of the membrane for hydrophobic contents (oil) of the mixture leading to the permeation of the oil alone, simultaneously separating the ethanol from the oil. The PA and PES membranes separated oil from oil/ethanol micelle based on particle size. Hence, in PA and PES membranes, there is a high probability of oil to permeate along with oil–ethanol micelle leading to increased oil loss and solvent content in the oil. The ability of PTFE membrane to effectively separate FFA from the oil was better compared to other membranes. The micelles formed when the oil is brought in contact with the ethanol led to the reduction in FFA in the oil by its inclusion into the micelles which are polar in nature and as a result they are easily separated by the hydrophobic nature of the membrane. This is very similar to the results obtained by Firman et al. [17], who found that polyvinylidene fluoride membranes effectively separated soybean oil from oil–hexane micelle by showing higher perselectivity. Also, Raman et al. [3] in his studies proposed the ideal use of hydrophobic membranes to effectively separate FFA from triglycerides.

4. Conclusions

Deacidification of sardine oil using PA, PES and PTFE was investigated in the present work. Of the three tested polymeric membranes, PTFE presented good separation results. It was seen that properties like oil fluxes, FFA reduction, oil loss and solvent removal were strongly influenced by feed pressure and concentration. The increase in oil/ethanol ratio caused a decrease in permeate flux of the oil. On the other hand, increase in the pressure caused an increase in permeate flux. PTFE membranes showed maximum efficiency in terms of FFA reduction, solvent removal and reduced oil loss. The use of membranes to assist the deacidification of sardine oil by solvent extraction gave promising results which could be considered for further applications in sardine oil refining. Although reasonable amounts of literature are available on the use of hydrophilic polymeric membranes, it is worth mentioning that the current study presents a future scope for the applications of hydrophobic membranes for the sardine oil deacidification in oil refining.

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