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EFFECT OF MEMBRANE DEGUMMING CONDITIONS ON PERMEATE FLUX AND PHOSPHOLIPIDS REJECTION

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Abstract

The objective of this study was to investigate the performance of PVDF membrane in degumming of undiluted crude soybean oil by using reverse osmosis/ultrafiltration module. The effects of membrane degumming conditions including temperature, membrane pressure, feed velocity, and volumetric concentration factor on permeate flux and phospholipids rejection were evaluated statistically. The effect of membrane pressure and volumetric concentration factor on the permeate flux was found to be statistically significant (P <0.05). An 86.11% rejection of phospholipids and average permeate flux of 17.04 L/m^2.h in total process were achieved at 40°C, 20 bar pressure, and 9L/min feed velocity. As the feed velocity increased to 18 L/min, phospholipids rejection and average permeate flux in total process were determined as 82.81% and 27.51 L/m^2.h, respectively. The flux behavior of PVDF membrane was also studied. Behavior of permeate flux with process time showed two separate regions namely; falling permeate flux region and constant permeate flux region. A second degree polynomial relationship was observed during falling permeate flux region; whereas a linear dependency was set for constant permeate flux region. A logarithmic equation was obtained when total process behavior was examined.

Keywords: Soybean oil, phospholipids, PVDF membrane, ultrafiltration

MEMBRAN DEGUMMING KOŞULLARININ PERMEAT AKISI VE FOSFOLİPİTLERİN REDDEDİLMESİ ÜZERİNDEKİ ETKİSİ

Öz

Bu çalışmanın amacı; ters osmos/ ultrafiltrasyon modülü kullanılarak soya yağına uygulanan degumming işleminde polivinilden fulorid (PVDF) membranın performansının araştırılmasıdır. Membran degumming işlem koşullarının (sıcaklık, membran basıncı, besleme hızı, hacimsel konsantrasyon faktörü) permeat akısı ve fosfolipitlerin reddedilme yüzdesi üzerindeki etkisi istatistiksel olarak incelenmiştir. Membran basıncının ve hacimsel konsantrasyon faktörünün permeat akısı üzerindeki etkisi istatistiksel olarak önemli bulunmuştur (P<0.05). Membran sıcaklığının 40°C, membran basıncının 20 bar ve besleme hızının 9L/dak olduğu koşullarda fosfolipitlerin reddedilme yüzdesi 86.11, tüm işlemde ortalama permeat akısı ise 17.04 L/m^2.s olarak belirlenmiştir. Besleme hızının 18L/dak değerine yükselmesi ile fosfolipitlerin reddedilme yüzdesi 82.81, ortalama permeat akısı ise 27.51L/m^2.s olarak saptanmıştır. Ayrıca PVDF membranın akı davranışı da incelenmiştir. Permeat akısının işlem süresi ile değişimi; akının sürekli düşme gösterdiği birinci bölge ve akının sabit kaldığı ikinci bölge olmak üzere iki bölgede tanımlanmıştır. Düşen akı bölgesi 2. dereceden polinomiyal, sabit akı bölgesi doğrusal, tüm işlem için logaritmik model geliştirilmiştir.

Anahtar kelimeler: Soya yağı, fosfolipitler, PVDF membran, ultrafiltrasyon

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INTRODUCTION

The removal of phospholipids (degumming) is the first step of crude oil conventional refining during which water, steam or dilute acids are added to convert phospholipids into hydratable forms that are insoluble in crude oil and these forms are removed from the crude oil by settling, filtering and centrifuging. The main drawbacks of this process are considerable loss of neutral oil and nutrients, large amounts of wastewater and fairly large energy consumption (Ochoa et al., 2001; Pagliero et al., 2001; Ulusoy et al., 2014; Sehn et al., 2016).

There has been interest in finding alternative methods to degum crude oils. Membrane degumming is one approach that offers advantages over conventional degumming, e.g., minimized the number of steps, process simplification, retention of all of the nutrients as well as other desirable components in the oil, low energy consumption, processing at ambient temperature, no addition of chemicals and low wastewater generation (Ochoa et al., 2001; Manjula and Subramanian, 2006; Roy et al., 2014; Niazmand et al., 2015; Vaisli et al., 2015).

Pressure-driven membrane processes are classified as reverse osmosis, nanofiltration, ultrafiltration and microfiltration depending on the nature of particles or molecular sizes of solute to be separated. Commercial membrane devices are available in four major types, namely plate and frame, tubular, spiral-wound, and hallow fiber (Manjula and Subramanian, 2006; Manjula et al., 2011; Akın et al., 2012).

In non-polar media like hexane or neutral oil, phospholipids molecules tend to form reverse micelles with an average molecular weight (MW) of 20,000 Daltons or more. This large MW enables the separation of phospholipids from either triglycerides (MW _ 800 Daltons) or triglyceride/hexane mixtures by ultrafiltration using appropriate membranes. Membrane processing has been applied to remove phospholipids from crude oil/hexane mixtures as well as from crude oil itself without addition of organic solvent. The main disadvantage of membrane degumming crude oil is low permeate flux due to the high oil viscosity (Pagliero et al., 2001). The main problem of membrane degumming crude oil/hexane mixtures is low membrane stability in hexane (Ulusoy et al., 2014). The interaction of the solvent with the membranes may result in swelling, lamination or dissolution of the membrane; this would subsequently cause structural changes to the membrane, leading to changes in the separation properties and reduced mechanical resistance to pressure (Sehn et al., 2016).

Membrane degumming process produces permeate and retentate fractions containing mostly triglycerides and phospholipids, respectively. Colored materials, some free fatty acids, and other impurities are also removed with the retentate fraction along with most of the phospholipids (Pagliero et al., 2001).

In this study, membrane degumming of undiluted crude soybean oil was investigated by using polyvinylidene fluoride (PVDF) ultrafiltration membrane. The effect of process conditions including temperature, membrane pressure, feed velocity, and volumetric concentration factor on permeate flux, and phospholipids rejection was evaluated statistically. Moreover, the changes in permeate flux with process time was studied mathematically.

MATERIALS AND METHODS

Crude soybean oil sample was purchased in a local oil refinery plant in Izmir-Turkey. The free fatty acid content, peroxide value, and phospholipids content of crude soybean oil were given in Table 1.

Table 1. The properties of crude soybean oil

Crude soybean oil	
Free fatty acid (oleic acid %)	1.52
Peroxide value (meqO_2/kg oil)	21.50
Phospholipids content (mg/kg oil)	2154

Free fatty acid content, peroxide value and phospholipids content of crude soybean oil were determined according to UIPAC Methods (UIPAC, 1982).

Polyvinylidene fluoride (PVDF) ultrafiltration tubular membranes with molecular weight cut-offs (MWCOs) of 20 kDa, and effective area of 0.0113m^2 were used (FPA03, ITT PCI Membranes Ltd, England) in membrane degumming process. Membranes were pre-treated by passing them water, water-ethanol mixture (50:50 v/v), ethanol, ethanol-hexane mixture (50:50 v/v) and hexane at 40°C, under increasing pressure (5, 10, 15, 20 bar) for 30 minutes.

Experimental runs were conducted in a reverse osmos/ultrafiltration system (Armfield FT-018). The module of membrane (PCI Membrane, MICRO-240) was useful for tubular membranes having 12mm diameter and 300mm length. Process temperature, feed velocity (max. 30L/min) and membrane pressure (max. 55bar) were controlled in the reverse osmos/ultrafiltration system.

Process temperature, membrane pressure, feed velocity and feed volume/retentate volume ratio (volumetric concentration factor, VCF, ml/ml) were determined as independent variables. Membrane degumming was carried out at 30°C and 40°C temperatures, 10 bar and 20 bar membrane pressures and 9 L/min and 18 L/min feed velocities. Each experimental run was duplicated. All data were the average of replicate experiments.

The effects of membrane degumming conditions on the performance of membrane were examined by determining the permeate flux (L/m^2.h) and rejection of phospholipids (%RP). The concentrations of phospholipids in feed and permeate were measured to determine the membrane phospholipids rejection defined as;

$\%RP = [\ 1 - (C_p\ /\ C_f)\ ]x100$

Where Cp and Cf were phospholipids concentration in permeate and crude oil, respectively.

In this study, the highest volumetric concentration factor was set at 5 and it was predicted that this value is sufficient for industrial scale use of the membrane degumming process (Lin et al., 1997).

All experiments and measurements were carried out duplicate, and the data were subjected to analysis of variance at a significance level of α =0.05.

RESULTS AND DISCUSSION

Effect of process conditions on permeate flux and phospholipids rejection

Figure 1 shows the change in the permeate flux as a function of process time at different temperature, membrane pressure and feed velocity levels. Permeate flux decreased with process time in all experiment combinations. A sharp decline in permeate flux was observed during the first few minutes, suggesting that fouling of the membranes is an important factor at the beginning of the process. The permeate 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. It was found that the effect of membrane pressure and VCF on the permeate flux was statistically significant (P <0.05) and that of the temperature and feed velocity were insignificant (P >0.05). As the membrane pressure was reduced from 20 bar to 10 bar, the permeate flux decreased rapidly at both temperatures (Figure 1). Related literature indicates that the process is pressure-driven at lower pressure applications; whereas it is certainly a mass transfer controlled process at higher pressure levels; which also was satisfied by the findings of this study. It is due to the consolidated gel layer on the membrane surface that the pressure independence of permeate flux was observed (Lin et al., 1997).

Changes in permeate flux, phospholipids content and percentage of phospholipids rejection with process conditions were given in Table 2.

VCF is the ratio of the initial feed volume to the retentate volume, and this factor indicates the degree of separation attained. Permeate flux decreased drastically with VCF (P <0.05). Moreover, VCF was not to be reached to 5 when the membrane degumming process was carried out at 30°C, 10 bar membrane pressure and 9 L/min feed velocity for 1200 minutes. The increase of retentate viscosity and extensive fouling of membrane at high VCF led to the decrease of permeate flux.

The effect of membrane degumming conditions on the phospholipids content and phospholipids rejection of soybean oil was statistically insignificant

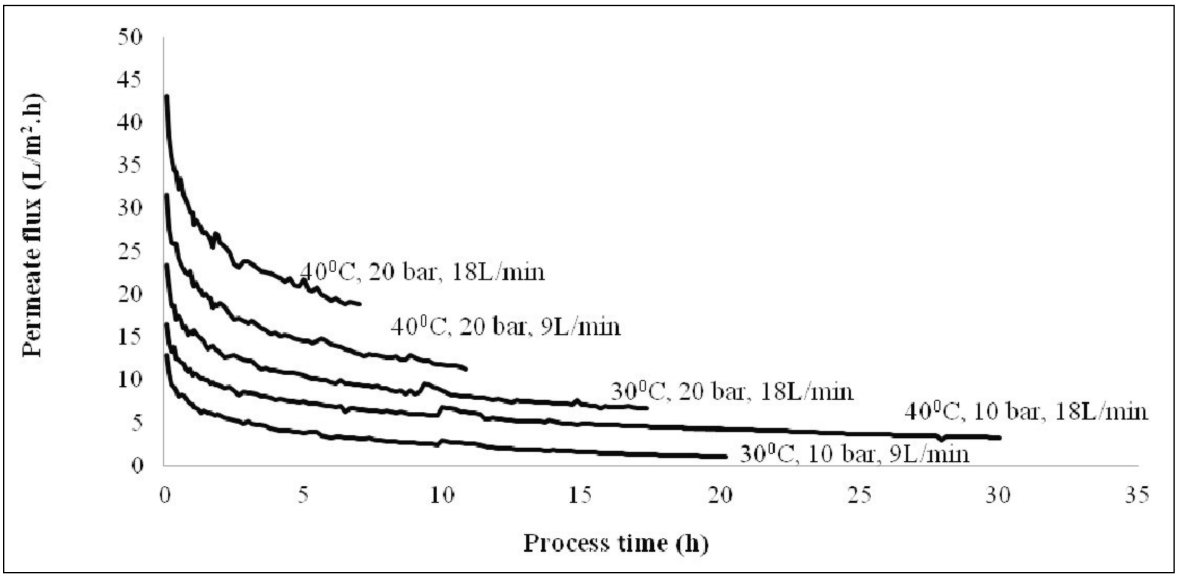

Figure 1. The change in permeate flux with process time

Table 2.The changes in permeate flux, phospholipids content and percentage of phospholipids rejection with process conditions

Temperature (°C)	Membrane pressure (bar)	Feed velocity (L/min)	VCF	Permeate flux (L/m².h)	Phospholipids content (mg/kg.oil)	Phospholipids rejection (%)
40	20	18	1	43.09	3750	82.59
40	20	18	3	20.69	3617	83.21
40	20	18	5	18.81	3702	82.81
40	20	9	1	31.56	3120	85.52
40	20	9	3	12.38	3049	85.85
40	20	9	5	11.19	2993	86.11
40	10	18	1	16.52	2734	87.33
40	10	18	3	4.01	2804	86.98
40	10	18	5	3.26	2760	87.19
30	20	18	1	23.35	2895	86.56
30	20	18	3	7.41	2878	86.64
30	20	18	5	6.61	2790	87.05
30	10	9	1	12.83	2580	88.02

($P > 0.05$). Phospholipids content of crude soybean oil was reduced from 21540 mg/kg to 2580-3750 mg/kg with membrane degumming and percentage of phospholipids rejection was calculated as 82.59-88.02% (Table 2). The molecular weight cut-off value for membranes, which is defined as the smallest molecular weight species for which the membrane has more than %90 rejections, plays a critical role in the maximum retention of phospholipids and permeate flux (Lin et al., 1997).

Flux behavior in PVDF membrane with undiluted crude soybean oil

The flux behavior of PVDF membrane was also studied with undiluted crude soybean oil. Behavior of permeate flux with process time showed two separate regions namely; falling permeate flux region and constant permeate flux region. A second degree polynomial relationship was observed during falling permeate flux region; whereas a linear dependency was set for constant permeate flux region. A logarithmic equation was obtained when total process behavior was examined (Table 3). Similar behaviors were reported for membrane degumming of mustard oil, groundnut oil, rice bran oil, sunflower oil and coconut oil (Araki et al., 2010; Manjula et al., 2011), sunflower oil (Pagliero et al., 2011), soybean oil (Firman et al., 2013) and macauba oil (Penha et al., 2015).

Table 3. The changes in process time, average permeate flux and permeate ratio for the falling permeate flux region, constant permeate flux region and total process and mathematical models

	40°C 20bar 18L/min	40°C 20bar 9L/min	40°C 10bar 18L/min	30°C 20bar 18L/min	30°C 10bar 9L/min
Falling Permeate Flux Region					
Process time (min)	0-55	0-200	0-330	0-90	0-250
Average permeate flux (L/m^2.h)	34.06	20.96	9.74	16.74	6.56
Permeate ratio^a (%)	28.00	41.58	30.37	15.02	42.10
Mathematical model	$y=0.16x^2-2.93x+44.42$ $R^2=0.93$	$y=0.01x^2-0.76x+29.83$ $R^2=0.95$	$y=0.004x^2-0.33x+114.91$ $R^2=0.95$	$y=0.04x^2-1.13x+29.83$ $R^2=0.91$	$y=0.005x^2-0.35x+10.87$ $R^2=0.92$
Constant Permeate Flux Region					
Process time (min)	60-420	210-650	340-1800	95-1040	260-1200
Average permeate flux (L/m^2.h)	23.24	13.39	4.71	9.06	2.21
Permeate ratio^a (%)	72.00	58.42	69.63	84.98	57.90
Mathematical model	$y=-0.25x+29.09$ $R^2=0.97$	$y=-0.10x+15.69$ $R^2=0.96$	$y=-0.03x+6.57$ $R^2=0.95$	$y=-0.07x+12.47$ $R^2=0.91$	$y=-0.03x+3.73$ $R^2=0.97$
Total Process					
Process time (min)	420	650	1800	1040	1200
Average permeate flux (L/m^2.h)	27.51	17.04	4.71	9.06	2.21
Total permeate volume (L)	1.902	1.897	1.879	1.89	0.684
Mathematical model	$y=-5.32\,\mathrm{Ln}(x)+51.09$ $R^2=0.99$	$y=-4.11\,\mathrm{Ln}(x)+38.15$ $R^2=0.99$	$y=-2.21\,\mathrm{Ln}(x)+19.92$ $R^2=0.99$	$y=-3.03\,\mathrm{Ln}(x)+27.75$ $R^2=0.99$	$y=-2.03\,\mathrm{Ln}(x)+15.41$ $R^2=0.99$

[a)] permeate ratio (%) = permeate volume (L) / total permeate volume (L)

Changes in process time, average permeate flux and permeate ratio for the falling permeate flux region, the constant permeate flux region and the total process were given in Table 3.

Falling permeate flux region was observed to be determinative when the entire process was considered in terms of process time, average permeate flux and permeate ratio. Hence; the stated process factors for this region was announced as critical factors in determining the efficiency of the overall process. Therefore; optimization for an efficient membrane degumming should be carried out at 400C temperature, 20 bar pressure and 18L/min feed velocity, when the phospholipids rejection, the average permeate flux, permeate ratio and the process time required for the VCF to reach 5 were considered (Table 3).

CONCLUSION

Results showed that the membrane degumming process applied on an industrial scale by using porous, tubular, ultrafiltration membranes with a large surface area was an alternative process to the conventional degumming operation. An 82.81% rejection of phospholipids and average permeate flux of 27.51 L/m2.h in total process were achieved at 40°C, 20 bar pressure and 18L/min feed velocity. The process time required for the VCF to reach 5 was determined as 420 min. It was also concluded that data achieved from undiluted crude oil as a result of this study were important in terms of further scale-up studies.

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