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Enrichment of Oryzanol in Rice Bran Oil by Composite Membrane

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Crude rice bran oil (CRBO) contains high levels of oryzanol, a bioactive shows many significant benefits for human health. The content of oryzanol in CRBO is relatively low for recovery by solvent extraction. Tthe refinery by chemical process also causes to lose a significant amount of oryzanol. Dense membranes can be applied for treatment of CRBO to refine the oil. The limitation of dense membranes is high resistant to permeate flux, consequently, very low capacity. In this research, the porous composite membrane was applied for enrichment of oryzanol, simultaneously, refinery of CRBO. The influences of temperature, pressure and adding of organic solvent (ethanol and n-hexane) on the separation of oryzanol, phospholipids (PL) and wax were conducted. Results show that, increase in temperature led to increase in oryzanol rejection. On the other hand, increase in operating pressure and adding of organic solvent caused decrease in oryzanol rejection. Under the operating conditions as the following: polypropylene membrane (HR98PP), ambient temperature, 50 bar and adding n-hexane with 4: 1 (w:w) of solvent: CRBO, at 1.73 of the concentration factor; the content of oryzanol in accumulative permeate was 1.8 g/L, consequently, increased 1.41 fold compared to the feed. More than 97 % of PL and wax were rejected from the feed. It means that, treatment of RBO by composite membrane is the potential technique for not only enrichment of oryzanol, but also refinery of CRBO.

1. Introduction

Oryzanol is a group of compounds containing ferulate esters of triterpene alcohols and plant sterol. It has been known as an antioxidant (Juliano et al., 2005), contributing to reducing low density lipoprotein (Sugano and Tsuji, 1997) and total serum cholesterol (Sasaki et al., 1990). Thus, it has been utilized as supplement in foods, pharmaceutical production, and cosmetic preparation. Rice bran oil has been known as a source of oryzanol, with 1 – 2 wt% of content. Recently, rice bran oil has been utilized in food industry as resource of lipid and antioxidant (Kaimail et al., 2002). The content of oryzanol in rice bran oil is low to utilize it as supplement or cosmetic preparation. Thus, it is necessary to enrich oryzanol in rice bran oil to enhance its adding value.

Recently, application of membrane technology in oil processing has been focused due to its advantages (Vaisali et al., 2015). Bhosle and Subramanian (2005) reported the application of dense membranes for deacidification of edible oil. Subramanian et al. (2001) have reported the feasibility of removing carotenoids from vegetable oil by using membrane. Membrane was also applied for decolorization of oil (Reddy et al., 2001). It was also applied for degumming of soybean oil (Ribeiro et al., 2008). Membrane technology has been applied for enrichment of oryzanol in rice bran oil. Manjula and Subramanian (2008) applied dense membrane for augmenting oryzanol content, reaching 1.55 fold higher than that in feed. Unfortunately, flux was low and process did not address to refinery of oil. Sereewatthanawut et al. (2011) applied nanofitration membrane to enrich oryzanol, integrating with removing free fatty acid (FFA). The content of oryzanol in product increased from 0.95 wt% in feed to 2.5 wt% in product after four diafiltraton volumes with oryzanol permeation yield of 80 %. In this method, a lot of organic solvent was used to dilute in nanofiltration process, that led to low economic efficiency. The rejection of PL and wax in the oil was not reported in that work.

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This research aimed to apply composite membrane for enrichment of oryzanol in rice bran oil. Using composite membrane can improve permeate flux, compared to dense membrane. It may simultaneously reject wax and PL in crude rice bran oil, which was not reported when using nanofiltration membrane.

2. Materials and methods

2.1 Materials

CRBO was extracted from rice bran, which is obtained from milling of rice in local factory, by n-hexane. Then, n-hexane in extract was removed by heating to obtain CRBO. After that, CRBO was degummed and dewaxed as the following procedure (Diosady et al., 1982): Heating CRBO to 75 °C, then, adding 2 % v/w of distilled water, keeping the mixture at 75 °C in 30 min, under 200 rpm of stirring speed. Then, adding 1 % w/l $CaCl_2$, followed by keeping at 75 °C in 30 min under 200 rpm of stirring speed. Then, the mixture was crystallized by cooling from 70 to 30 °C at 0.4 °C/min of cooling rate. After that, the mixture was centrifuged to remove gum and wax at 3,000 rpm of speed. The characteristics of CRBO was as the following: moisture: 0.05±0.003 wt%, PL and wax: 0.94±0.06 wt%, oryzanol: 1.25±0.01 wt%, free fatty acid (FFA): 5±0.5 wt%.

2.2 Membrane apparatus

A bench scale membrane separation unit (Model HP4750, Sterlitech, USA) was utilized for filtration of CBRO. It is stirred cell equipped circular membrane (4.9 cm of diameter and 14.6 cm^2 of effective area) (Figure 1). The speed of stirrer was 200 rpm. Pressure was supplied by nitrogen gas. Membrane was HR98PP –RO, manufactured by Alfa Laval (Denmark). It is porous composite membrane made from polypropylene. Volume of feed was 200 mL.
Observed rejection (R, %) was expressed as the following equation (Manjula and Subramanian, 2008):

$$R = \frac{100 \ln{(C_{R,f}/C_{R,i})}}{\ln{(W_i/W_f)}} \quad (1)$$

Where, $C_{R,i}, C_{R,f}$ are the initial and final concentrations of solutes in the retentate (g/L of oil), and W_i, W_f are the the initial and final volume of oil in retentate.

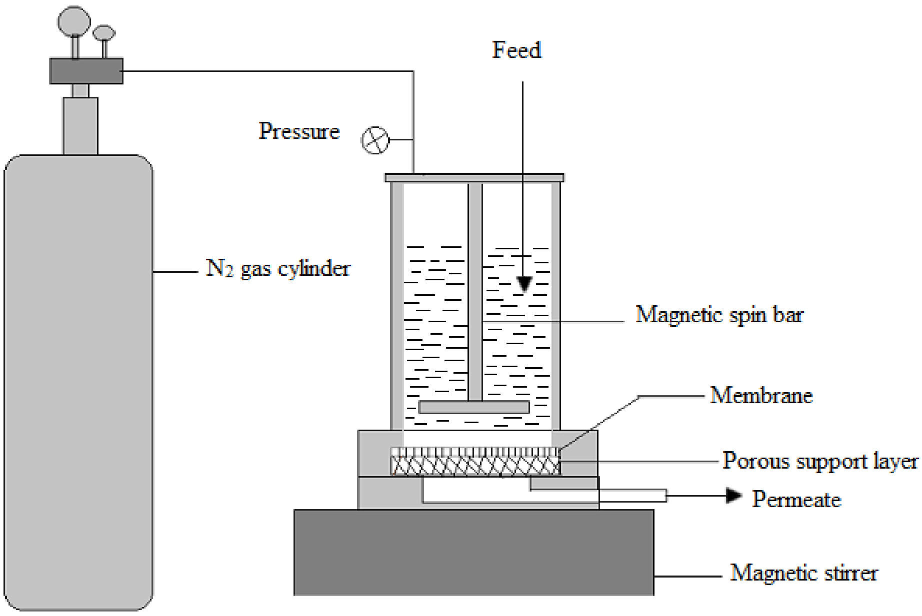

Figure 1: Sterlitech HP4750 Stirred Cell

2.3 Methods of analysis

Oryzanol content in oil was determined by spectrophotometric method at a wavelength of 315 nm of the solution in hexane (Seetharamaiah and Prabhakar, 1986). PL and wax content were determined by the method proposed by De and Bhattacharyya (1998). FFA was determined by method followed AOCS (Firestone, 1997).

3. Results and discussion

3.1 Influence of temperature on filtration of CRBO by HR98PP

Permeate flux of undiluted CRBO and rejection of oryzanol in filtration by HR98 PP at 40 bar of operating pressure under different temperature is shown in Table 1. Result indicated that, CRBO could not pass through membrane HR98PP membrane at ambient temperature. Increase in temperature of CRBO caused increase in permeate flux. There are 2 mechanisms for solutes to pass through membrane: solution – diffusion and convection (Bhattacharyya and Williams, 1992). It means that, permeate flux of components depends on the solubility and diffusivity of them in membrane and rate of convective flow. The solution-diffusion is significantly predominant, compared to convection. Diffusivity depends on the viscosity of solution, according to Wike – Chang equation: lower viscosity lead to higher diffusivities (Kagaku, 1999). Thus, increase in temperature led to decrease in viscosity, consequently, increase in diffusion of oil through membrane.
Result also indicated that increase in temperature caused increase in rejection of oryzanol from CRBO. Oryzanol includes campersteryl, 2,4-methylene cycloartanyl, cycloartenyl and β-sitosteryl ferulate. Its polarity is higher than that of triglyceride. Besides, the active surface of RO-HR98PP membrane is hydrophobic. Thus, triglyceride permeated preferentially through the membrane and oryzanol was remained in the retentate; even though molecular weight of oryzanol (~600 Da) is smaller than that of triglyceride (~800 Da) (Bockisch, 1998). Oryzanol would have affinity for other polar components, such as PL, thus oryzanol attached to hydrophilic polar heads of PL resulting in increasing size and polarization of the compounds (Manjula and Subramanian, 2008). Thus, it remained oryzanol in retentate. Experimental result shown that, rejection of PL and wax was approximately 100 %, it means that PL and wax remained in retentate. According to increase in operating temperature, diffusion and convection of triglyceride through membrane was higher than in oryzanol, thus, rejection of oryzanol increased.
The obtained result indicated that, with CRBO, in order to enrich oryzanol, it required to heat the oil, consequently, higher consumption of energy. Experimental result also indicated that, PL and wax remained in oryzanol enriched oil.

Table 1: Influence of temperature on filtration of CRBO by HR98PP

T (ºC)	R (%)	J ($L.m^{-2}.h^{-1}$)
Ambient	-	0
40	20.28	0.19
60	31.86	0.26

3.2 Influence of dilution by organic solvents in filtration of CRBO by HR98PP

In order to improve the performance of RO filtration of CRBO, the influence of dilution of CRBO with n-hexane and ethanol was investigated. Ethanol and n-hexane were chosen because ethanol and n-hexane are the typical polar and non-polar organic solvents. Permeate flux of diluted CRBO system is shown in Figure 2a. Increase in dilution of CRBO by organic solvent led to increase in total permeate flux (including oil and solvent). It can be explained by Wilke-Chang equation (Kagaku, 1999). The dilution with organic solvent caused the reduction of viscosity. Thus, the more dilution is, the higher total permeate flux is. Total permeate flux of CRBO – n-hexane system was higher than that of CRBO-ethanol system. At ambient temperature, viscosity of n-hexane and ethanol is 0.28 and 0.98 mPa.s. Polarity of n-hexane is lower than one of ethanol. Consequently, it enhanced the diffusion of system through HR98PP, a hydrophobic membrane.
Dilution of CRBO with organic solvent could make the triglyceride pass through HR98PP at ambient temperature. It can be explained that, with the dilution, the convection of flux forced triglyceride to pass through membrane. The permeate flux of oil was contributed by convection, because the result in Figure 2a shows that it insignificantly changed with change in viscosity and polarity of system (Bhattacharyya and Williams, 1992,). The dilution with n-hexane led to higher oil flux, compared to dilution with ethanol. The convective flow in CRBO – n-hexane system was higher than that in CRBO – ethanol system, thus, forced more oil to pass through membrane.
The rejection of oryzanol in RO filtration of diluted CRBO is shown in Figure 2b. In both cases, dilution caused decrease in rejection. The minus rejection indicates that, the content of oryzanol in oil of permeate side was higher than that in oil in retentate side. In undiluted CRBO, oryzanol combined with PL. Thus, it remained in retentate. When diluting with organic solvent, oryzanol dissolved in solvent and passed through membrane. Oryzanol dissolves in n-hexane better than in ethanol (Saravanan et al., 2006). Thus, oryzanol in CRBO – n-hexane passed through hydrophobic membrane better than in CRBO – ethanol system. It means that, rejection of oryzanol in CRBO – n-hexane was lower than that in CRBO-ethanol system.

When dilution with organic solvent, flux of total permeate increased. It means that, the contribution of convection into the motion of oryzanol through membrane increased (Bhattacharyya and Williams, 1992), consequently, rejection of oryzanol reduced. Thus, rejection of oryzanol decreased with increase in dilution. The minus rejection indicates that, the contribution of diffusion into the motion of oryzanol through hydrophobic membrane is insignificant. In this experiment, the rejection of PL and wax was approximately 100 %. It means that the refinery of oil from PL and wax was also obtained.

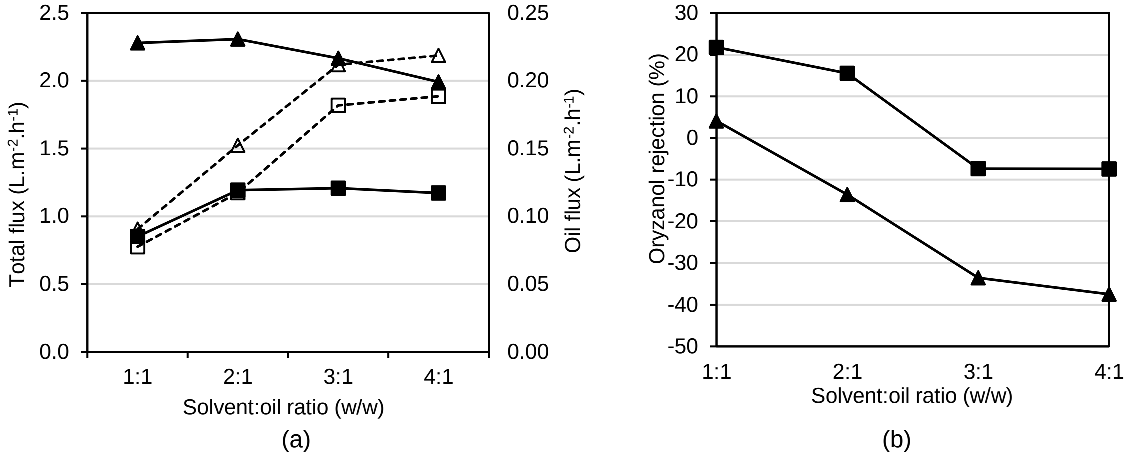

Figure 2: Influence of dilution (a) on flux in RO filtration of CRBO (▲: CRBO – n-hexane, ■: CRBO – ethanol, filled plot: total flux, unfilled plot: oil flux) and (b) on oryzanol rejection in RO filtration of CRBO (▲: CRBO – n-hexane, ■: CRBO – ethanol).

3.3 Influence of operation pressure in filtration of CRBO by HR98PP

The influence of pressure on permeate flux in RO of CRBO – n-hexane system with 4:1 (w/w) of dilution ratio was shown in Figure 3a. Increase in operating pressure led to shown increase in total flux and oil flux through membrane. The relationship between operating pressure and fluxes was linear. It means that, increase in operating pressure did not lead to changes in total resistant to permeate (Bhattacharyya and Williams, 1992).
Influence of operating pressure on rejection of oryzanol in RO of CRBO – n-hexane system is shown in Figure 3b. Increase in operating pressure led to decrease in rejection of oryzanol. It can be explained that, increase in operating pressure caused increase in convection of flux, consequently, enhanced motion of oryzanol through membrane (Saravanan et al., 2006).

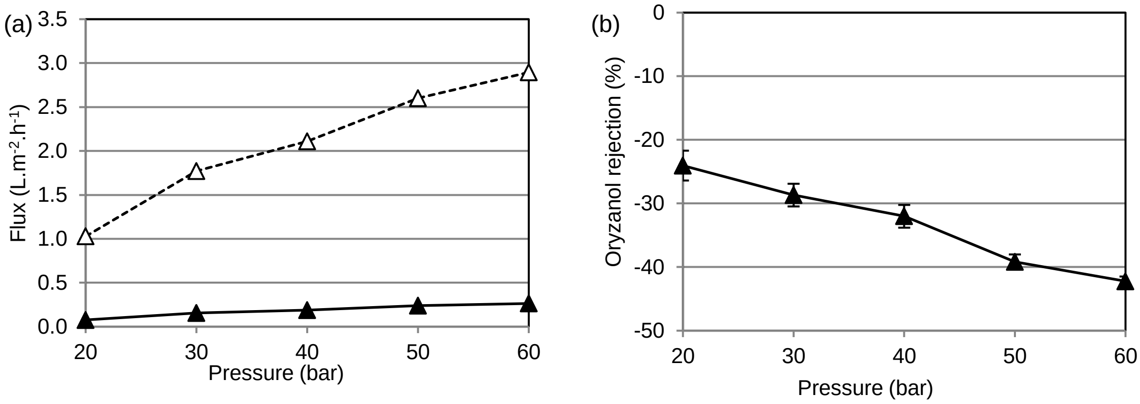

Figure 3: Influence of operating pressure (a) on flux in RO filtration of CRBO (filled plot: total flux, unfilled plot: oil flux), (b) on oryzanol rejection in RO filtration of CRBO

3.4 Filtration process of CRBO

The process of RO of CRBO-n-hexane system by HR98PP membrane at 40 and 50 bar of operating pressure was investigated with ratio of n-hexane:CRBO being 4:1 (w:w). Total and oil flux against the concentration factor (ratio of initial volume to retentate volume) was shown in Figure 4a. With increase in concentration factor, total flux and oil flux reduced. It can be explained that, in process, there was the fouling causing by adsorption of matters on membrane surface and wall of pores (Subramanian et al., 2001). The fouling led to increase in resistant, consequently, reducing the permeability of flux.

Rejection of oryzanol in RO process of CRBO- n-hexane is shown in Figure 4b. It can be divided into two sections: significantly reduction in early state of process, then slightly increase in later section. This phenomenon was caused by the change in total flux in RO process (Bhattacharyya and Williams, 1992). The rejection of FFA was also minus and approximate with that of oryzanol. Koike et al. (2002) proposed that, the approximation of molecular size of FFA with that of oryzanol, although molecular weight of FFA (256 – 282 Da) is significantly smaller than that of oryzanol (600 Da), led to insignificant difference in rejection of them. Result also means that, FFA in permeate was higher than that in retentate. Thus, it could not improve the acid value of CRBO in permeate. In order to remove FFA, it is necessary a further process for refinery using nonporous membrane (Manjula and Subramanian, 2008).

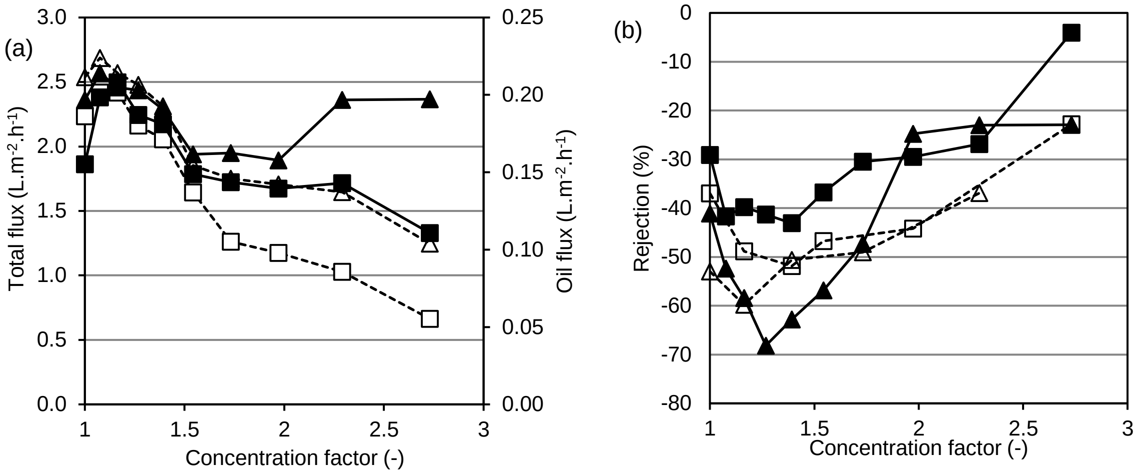

Figure 4: : Influence of RO filtration process on (a) flux of CRBO (▲: at 50 bar, ■: at 40 bar, filled plot: oil flux, unfilled plot: total flux, (b) on rejection of CRBO (▲: at 50 bar, ■: at 40 bar, filled plot: oryzanol, unfilled plot: FFA).

At 1.73 of concentration factor of CRBO – n-hexane system (1.27 of oil), content of oryzanol in oil in permeate side was approximately 18 g/L. It was 1.41 fold higher than that in feed. In addition, content of PL and wax was analysed and result indicates that it was remained in retentate. Result indicated that, FFA content in oil in permeate was higher than in feed. Thus, it is necessary to refine oryzanol-enriched oil by an appreciate process to remove FFA. The summary of mass balance was shown in Figure 5.

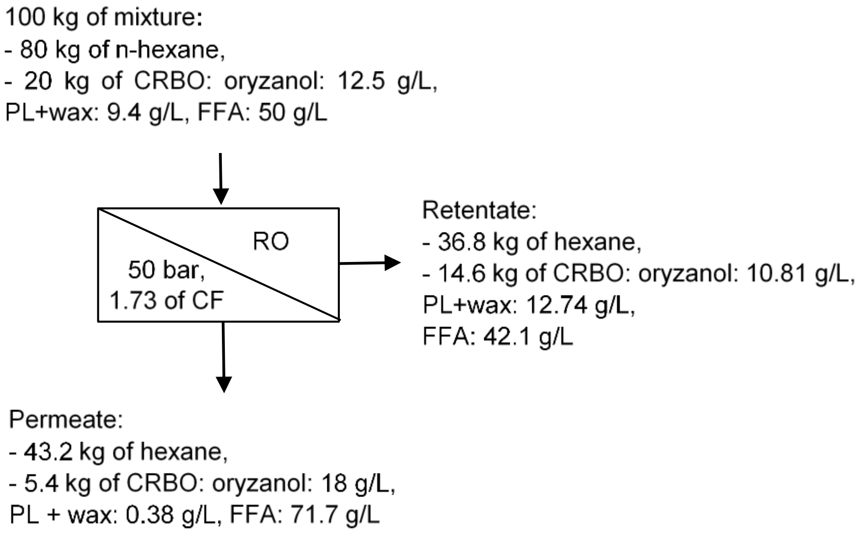

Figure 5: Mass balance of RO process of CRBO at 1.73 of concentration factor of CRBO – n-hexane system.

4. Conclusions

Porous composite membrane demonstrated the high capacity of separation of oryzanol in CRBO. Content of oryzanol increase from 1.2 % to 1.8 % in rice bran oil. Adding n-hexane to CRBO improved oil flux and oryzanol through membrane, consequently, enhance oryzanol content in oil. The obtained oil contained low PL and wax. Result shown that, porous composite RO membrane is potential to apply for enrichment of oryzanol and refinery of CRBO.

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