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Preparation of Deoiled Soy Lecithin by Ultrafiltration

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Abstract Deoiling of soy lecithin through ultrafiltration (UF) using an inorganic ceramic membrane was examined in a favorable solvent medium (hexane). Phospholipid (PL) reverse micelles with an average particle size of 9.8 nm were prepared in a 1:3 soy lecithin/hexane system (m/m) with 9% water added at a temperature of 25 °C. Consequently, an inorganic ceramic membrane with a pore size of 5 nm was selected. UF was employed in continuous diafiltration mode at transmembrane pressure (TMP) of 0.25 MPa, and a final deoiled lecithin product with a high acetone insoluble (AI) content of 96.32% was obtained at a yield of around 84%.

Keywords Deoiled lecithin · Ultrafiltration · Phospholipid reverse micelles · Acetone insoluble matter

Introduction

Deoiled lecithin is well recognized for its excellent surface-active properties and has thus found extensive uses in food, cosmetics, pharmaceutical, medicinal, and industrial applications [1]. Conventional preparation of deoiled lecithin from crude soy lecithin is based on acetone extraction utilizing the difference in solubility between phospholipid (PL) and triacylglycerols (TAGs). However, this process normally involves repeated extraction procedures that consume large amounts of acetone; in addition, residual acetone in the final products poses potential hazards to consumers [2]. An alternative process to acetone extraction is supercritical fluid extraction (SCFE), which requires pure CO_2 at pressures as high as 60–100 MPa [3–5]. As the viscosity of the lecithin increases during the deoiling process, the efficiency with which oil is removed becomes unsatisfactory. Although propane can be used as an entrainer along with CO_2 to maintain the lecithin in a liquid state so as to obtain an oil-free product [4], SCFE is still hindered from large-scale applications due to the very high costs associated with the capital-intensive equipment necessitated by the high pressure and long production cycles. Thus, the need is growing to develop safer, more efficient, and more convenient processes for industrially separating lecithin from oil.

Membrane separation technology, whose practical application dates from the 1960s for desalination of seawater [6], has been widely applied in the food processing area for concentration, fractionation, and purification purposes due to its acceptable energy and cost efficiency. Membrane technology has also been introduced into the oil industry, although most applications are focused on refining, such as degumming, deacidifying, and decoloring [7–9]. So far to our knowledge, a rather limited number of attempts have been made towards employing membrane separation for deoiling lecithin [10, 11]. An ultrafiltration-based process was developed in 1998 by Archer Daniels Midland Company (ADM, USA) using polyvinylidene fluoride membrane with a molecular weight cut-off (MWCO) of 10–50 kDa, which produced deoiled lecithin with a 90% AI content [10], a relatively high purity, although not reaching the deoiled lecithin standard set by the Central Soya Company [11]. A nonporous membrane based on the diafiltration process has also been used in deoiling lecithin [12], resulting in an increase in the AI

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content of soy lecithin from 63.2 to 81.0% in a single-step batch operation. Nonporous membranes were able to reject PL reverse micelles as well as their monomers. However, both processes exhibited rather low membrane flux and low resulting deoiled lecithin productivity, which hindered their applicability for commercial uses.

Phospholipids are surfactants in nature; due to their hydrophilic and hydrophobic ends, they form reverse micelles with globular structure under certain conditions in a nonaqueous environment [8]. The purpose of this study was to develop an inorganic, ceramic membrane-based process for deoiling soy lecithin using water to facilitate formation of PL reverse micelles, so as to improve the deoiling efficiency of the membrane process. The tasks included optimizing a set of parameters for forming PL reverse micelles in a lecithin–hexane system by adding water so as to achieve size distributions of PL reverse micelles large enough for ultrafiltration and establishing conditions for the subsequent membrane separation.

Materials and Methods

Materials

Soy lecithin [color: red brown; AI content: 62.82%; hexane insoluble (HI) content: 0.024%; moisture: 0.18%; acid value (AV): 20.42 mg KOH/g; peroxide value (POV): 1.8 meq/kg) was obtained from Bohi Oils & Fats Industrial. (Shandong, China); *n*-hexane and acetone of analytical purity were purchased from Sinopharm Chemical Reagent (Shanghai, China).

Methods

PL Reverse Micelles Formation

The PL reverse micelles were prepared under designed conditions using different lecithin-to-hexane mass ratios (1:1,1:3,1:5,1:10), water amounts (0, 1, 3, 6, 9, 12%), and temperatures (25, 40, 60 °C). The size distributions of PL reverse micelles were determined by a Zetasizer 3000HS dynamic light scattering particle size analyzer (Malvern Instruments, UK).

Membrane Separation

The ultrafiltration experiments were carried out on a lab-scale ZF ultrafiltration module using tubular inorganic ceramic membranes made of α-Al$_2$O$_3$ (Hunan Ever-Shine Pro-environment Industry, China). The membranes were 25 cm in length with a filter area of 0.04 m^2, having 19 channels with an internal diameter of 4 mm. The membrane

pore diameters were 5, 20, and 50 nm, respectively. Transmembrane pressure (TMP) ranged from 0 to 0.35 MPa, and the ultrafiltration temperature was 25 °C. The experiments were performed with 1 kg lecithin-hexane mixture each time and the performance of the membrane process was expressed in terms of permeate flux (L m^{-2} h^{-1}). Furthermore, the effects of three modes of operation were studied, including single diafiltration, continuous diafiltration, and discontinuous diafiltration. In single diafiltration, no solvent was added during the operation, and the lecithin-hexane mixture was processed until a desired volume-to-concentration ratio (VCR) was reached. During discontinuous diafiltration, hexane and water in fixed proportion were compensated every hour according to the volume of penetrates. In continuous mode, constant hexane and water in fixed proportion were added during the operation. Each operation was conducted for 3 h. After each diafiltration, the membrane module was cleaned with 1% sodium hydroxide solution for 20 min, according to the manufacturer's recommendations.

Retentate Post-Treatment

Most solvent in retentate was removed on a rotary evaporator at 55 °C, 0.09 MPa, and 100 rpm for 30 min; the concentrated product was then dried at 55 °C under vacuum (101.3 KPa) for 4 h.

Routine Analysis

The feed, retentate, and permeate were analyzed by the following AOCS official methods [13]: hexane insoluble matter: Ja 3-87; AI matter: Ja 4-46; acid value: Cd 3d-63; peroxide value: Cd 8-53.

Results and Discussion

PL Reverse Micelles Formation

Effect of Solvent Ratio

Phospholipids are surfactants in nature; they have both hydrophilic and hydrophobic ends and form reverse micelles with globular structure in a nonaqueous environment when the PL concentration is greater than a critical micelle concentration (CMC) of 0.01% under the given conditions (hexane-soybean oil system 70/30 v/v, temperature 25 °C, and water amount 0.18%) [14]. Size distributions of the resulting PL reverse micelles in a binary mixture of soy lecithin and hexane at different mass ratios are shown in Fig. 1. As shown in Fig. 1, the sizes of PL reverse micelles in the system are rather small, generally
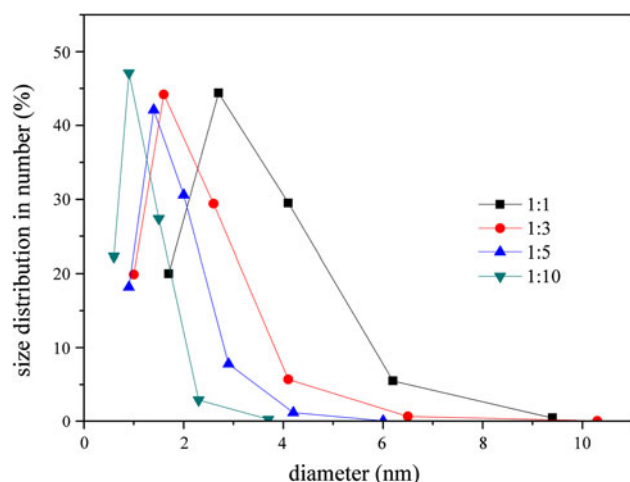
Fig. 1 Particle size distribution of PL reverse micelles in relation to lecithin-to-hexane mass ratio (temperature: 25 °C)

Fig. 2 Particle size distribution of PL reverse micelles in relation to water addition (temperature: 25 °C; lecithin-to-hexane mass ratio: 1:3)

less than 5 nm. As the mass ratio of lecithin-to-hexane decreased, the corresponding sizes of the reverse micelles decreased. This phenomenon can be explained by the inadequacy of water in the lecithin-hexane system to provide the required central core of micelles, as the commercial soy lecithin contained only 0.24% moisture. When the lecithin-to-hexane mass ratio increased, the resulting lower PL concentration led to the occurrence of single PL molecules or small aggregates, as reflected by the large proportion of micelles around 1 nm [15]. When the proportion of hexane decreased, the concentration of PL increased, and the small PL molecules began to interact. The hydrocarbon chains of PL thus may overlap, resulting in accumulation of PL molecules with increased particle sizes; yet the rate of increase is very limited. Considering the viscosity of the lecithin-hexane system, 1:3 was selected as the suitable mass ratio in the subsequent experiments.

Effect of Adding Water

To prepare PL reverse micelles of the proper particle size for membrane separation in this study, water was added to the lecithin-hexane system (lecithin-to-hexane mass ratio: 1:3) in amounts ranging from 1 to 12%; the resulting size distributions of PL reverse micelles are shown in Fig. 2. The average particle size of PL reverse micelles showed an increasing-decreasing trend as the amount of water increased. The particles increased from 2 to 10 nm when water addition increased from 0 to 9%; the maximum was reached at a water addition of 9%, when more than 98% of the micelles were greater than 5 nm. The reason for this phenomenon might be that there was a central water core in the PL micelles; as the amount of water increased, the PL
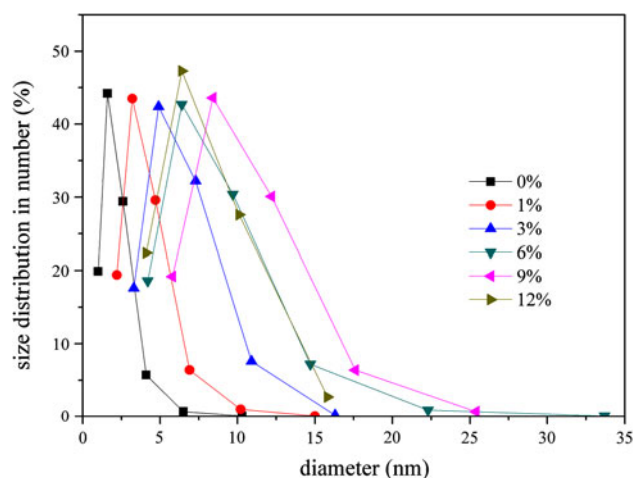
hydrophilic head was able to absorb more water, resulting in the greater size of PL micelles. However, when the water content reached 12%, the average particle size of the micelles decreased markedly from 9.8 to 7.2 nm, probably due to the saturation of the hydrophilic heads of PL by water molecules and the increased free energy in the system associated with excess water. In order to reduce free energy, larger PL micelles might be disintegrated to parcel more water droplets, which made the average PL micelles size smaller. Thus, 9% was selected as the suitable amount of water to be added in the following experiment.

Effect of Temperature

To prepare PL reverse micelles of the proper particle size for membrane separation, temperatures ranging from 25 to 60 °C were also tested in the lecithin-hexane system with a mass ratio of 1:3 and 9% water added. The size distributions of PL reverse micelles are shown in Fig. 3. As shown in Fig. 3, the average PL micelle size decreased when the temperature increased, although to a small degree. Theoretically, the impact of temperature on PL reverse micelle sizes is very complex [16]. Higher temperatures encourage PL micelles to swell, and thus the particle sizes of micelles become larger. On the other hand, as the temperature increases, the thermal motion of the molecules increases so that the formation of micelles is hindered. From the results discussed above, the destructive effects of too high temperatures may be predominant, making PL reverse micelles shrink. Considering also the volatility of hexane and the system liquidity, 25 °C was selected as the suitable temperature for the formation of reverse micelles.
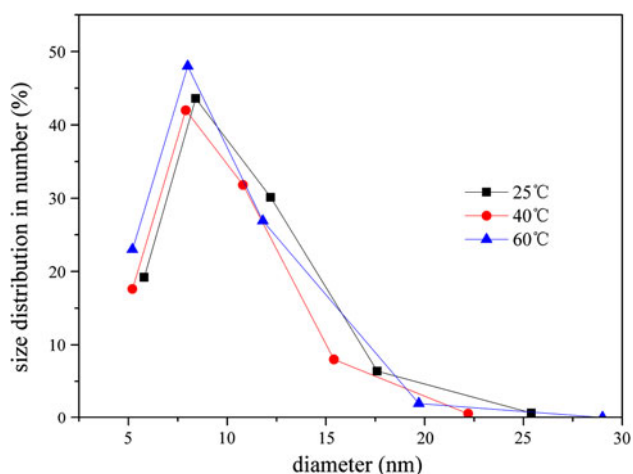
Fig. 3 Particle size distribution of PL reverse micelles in relation to temperature (lecithin-to-hexane mass ratio: 1:3; added water: 9%)

Membrane Separation Conditions

Membrane Selection

The pore size of membranes, which is defined as the smallest molecular size for which the membrane has more than 95% rejection, plays a critical role in maximizing retention [17]. Based on the results above, the following conditions were selected for preparing PL reverse micelles: lecithin-to-hexane mass ratio 1:3, water addition 9%, and temperature 25 °C, which produced PL reverse micelles with an average particle size of 9.8 nm, with 98% being greater than 5 nm (Fig. 3). Thus, an inorganic ceramic membrane with a pore size of 5 nm was selected for preparing deoiled lecithin. Considering the concentration polarization and membrane fouling [18], membranes with bigger pore sizes, i.e., 20 and 50 nm, were also tested in
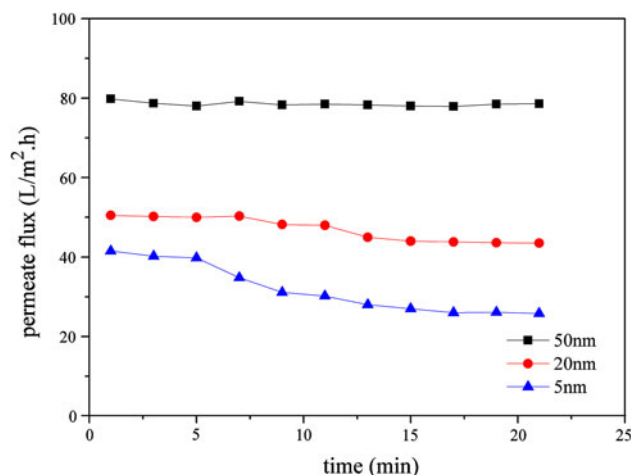

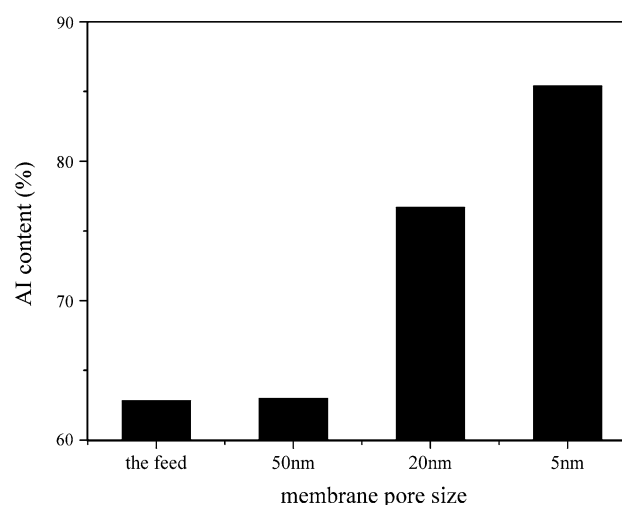Fig. 4 Permeate flux of three membrane pore sizes in relation to operation time

Fig. 5 AI content of retentates in relation to membrane pore size

this study. Figure 4 shows the permeate flux-time curves for the three membranes employed. Obviously, the bigger the pore size was, the larger the average permeate flux was. The permeate flux of the 50 nm membrane showed few changes with time and that of the 20 nm membrane showed a small decrease after 10 min diafiltration. In contrast, that of the 5 nm membrane showed a remarkable flux decline after 5 min diafiltration and became stable until 15 min, which indicated that the 5 nm membrane could reject PL reverse micelles effectively. Moreover, AI contents of the retentates of each membrane are shown in Fig. 5. The AI content of the retentate decreased as the membrane pore size increased. The 50 nm membrane showed little efficiency in deoiling; the 20 nm membrane showed greater efficiency but still not satisfactory, while the AI content of the retentate of the 5 nm membrane improved from an initial level of 62.82% to a high level of 85.40%, which showed a high efficiency in deoiling. Therefore, the membrane with a pore size of 5 nm was selected for preparing deoiled lecithin.

Effect of Pressure

Effects of TMP on permeate flux are shown in Fig. 6. As TMP increased from 0 to 0.25 MPa, the permeate flux showed a sharp increase. When TMP was higher than 0.25 MPa, permeate flux remained stable. The membrane separation process is pressure-controlled at low TMP, with the membrane permeate flux rapidly increasing as TMP increases; however, at high TMP, due to fouling in the membrane pore channels and layer forming on the membrane surface caused by concentration polarization, the membrane resistance increases and the separation process changes to a mass transfer-controlled stage, where the membrane permeate flux changes less prominently. Similar
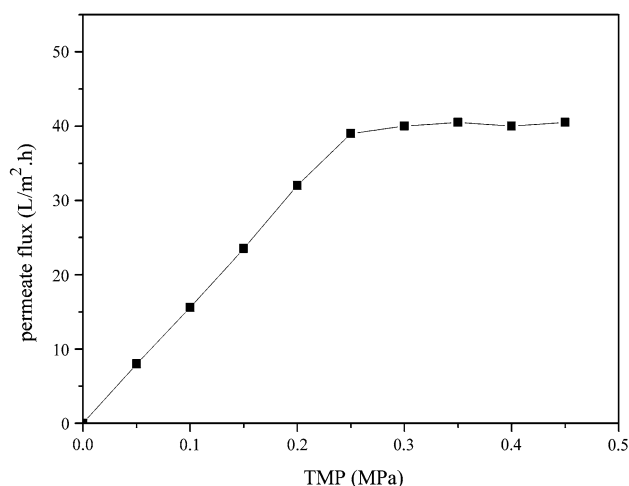
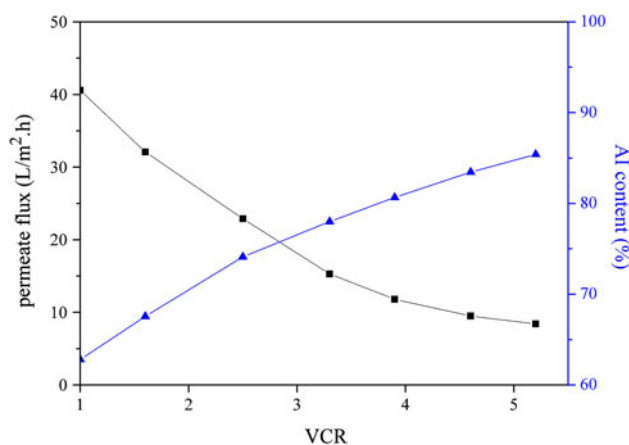**Fig. 6** Permeate flux in relation to transmembrane pressure

Fig. 7 Permeate flux and AI content of retentate in relation to VCR

behavior was noted by Kim et al. [19], who studied the influence of three different concentrations of soybean oil in hexane during degumming by UF, using polyimide membranes with an MWCO of 20 kDa. The point at which the membrane separation process changes from the pressure-controlled stage to the mass transfer-controlled stage is known as the critical pressure, which is considered as the suitable TMP for ideal membrane separation [20].

Accordingly, 0.25 MPa was determined to be the critical pressure and thus the operating pressure in the diafiltration for preparing deoiled lecithin.

Mode of Membrane Separation

In single diafiltration, the lecithin-hexane mixture was processed until a desired VCR over 5 was reached after a 3 h operation period. In Fig. 7, the permeate flux decreased continuously as VCR increased, which can be explained by concentration polarization phenomena caused by the increasingly higher viscosity of the retentate. The AI content in the retentate kept rising with the VCR, indicating that VCR can characterize the extent of membrane processing.

The performances of three operations are presented in Table 1. AI measurement is a simple and rough measure of PL and can roughly reflect purity of crude and deoiled lecithin. The level of AI content in retentate obtained in a single diafiltration was not very high (85.40%); lecithin with a higher AI content (>95%) would be preferred in most applications owing to the great purity and lower oil content. In order to improve the performance of the membrane process, discontinuous diafiltration and continuous diafiltration were undertaken, respectively. As a consequence, the AI content of retentate improved from the initial level of 62.82 to 90.20% in discontinuous diafiltration. Continuous diafiltration produced the best deoiled lecithin, with an AI content as high as 96.32%, reaching the standard of deoiled lecithin set by the Central Soya Company. It seems that it is possible to increase the AI content further with a corresponding decrease in the oil content in deoiled lecithin by increasing the solvent volume during diafiltration. In addition, continuous diafiltration of the lecithin-hexane mixture can help reduce the viscosity of the feed sample from the start of the operation and enable a higher permeation rate in comparison to single diafiltration and discontinuous diafiltration, thus enhancing the processing efficiency.

Yield is defined as the amount of AI matter in deoiled lecithin divided by the AI matter in crude soy lecithin,

Table 1 Membrane deoiling of soy lecithin

Sample	Color	AI[a] (%)	HI[a] (%)	Yield (%)
Crude soy lecithin	Red brown	62.82	0.024	–
Retentate in single diafiltration	Yellow	85.40	0.043	67.25
Retentate in discontinuous diafiltration	Yellow	90.20	0.032	78.68
Retentate in continuous diafiltration	Yellow	96.32	0.039	84.12
Standard of Central Soya, USA	Yellow	>95	<0.3	–

AI Acetone insoluble content, *HI* hexane insoluble content

[a] Hexane-free basis

which can roughly represent PL productivity. Yield in continuous diafiltration was the highest (84.12%), which already reflected a remarkable reduction in PL. PL reduction during these diafiltrations was mainly due to PL adsorption losses on the membrane surface and in the membrane pores. In addition, there was more PL lost into permeates in single diafiltration as the sizes of PL reverse micelles in the mixture decreased as the hexane amount decreased and the water amount correspondingly increased during the operation. The solvent amount was kept constant by continuous or discontinuous addition of solvent during the other two diafiltrations, which maintained the optimum conditions for the formation of PL reverse micelles. The results revealed that continuous diafiltration can obtain not only the ideal purity but also the ideal productivity.

Conclusion

The present work demonstrates that by using a suitable lecithin-to-hexane mass ratio and added water at room temperature, PL reverse micelles can be formed in ideally large sizes. Consequently, by means of UF using an inorganic ceramic membrane with a suitable pore size working under critical pressure in continuous diafiltration, a final deoiled lecithin product with a high AI content of 96.32% was obtained at a yield of around 84%. These encouraging results, although on a laboratory scale, offer an alternative direction to developing newer processes for lecithin purification.

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