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学 位 論 文 題 名

Nanofiltration for Recovering Benzoic Acid from Cranberry Juice

（クランベリージュースから安息香酸を抽出するナノろ過技術）

学位論文内容の要旨

Benzoic acid (C_6H_5-COOH, M=122, pK_a = 4.21) is an antibacterial preservative used widely in food and cosmetic industries. Recently, it is produced by oxidation of toluene with following drawbacks: high energy consumption, high impurities, and high production cost. Thus, it is necessary to look for an alternative source which is cheap and friendly with human health to produce benzoic acid for using as a natural preservative in food and cosmetic industries. Benzoic acid naturally occurs in cranberry (*Vaccinium macrocarpon*) with high concentration. The total content of benzoic acid (both in the free and bound states) in fresh cranberry juice is 178 ppm. Therefore, if benzoic acid is recovered from cranberry juice with low cost, it can be used as a natural preservative.

Nanofiltration is a pressure-driven membrane process with molecular weight cut off (pore size) situating between ultrafiltration and reverse osmosis membranes. It has been widely applied in food industry because of the low operating temperature; consequently retain the natural quality of products, and low cost for energy. Moreover, it is easy to install, operate and maintain a nanofiltration system. The separation of solutes by nanofiltration is achieved by sieving mechanism (steric effect) and electrical exclusion. Comparing with other components in cranberry juice, for example: sugars, malic acid, citric acid, quinic acid, anthocyanins etc., benzoic acid exhibits the differences in molecular size and electrical charge. Therefore, nanofiltration can be applied for separation of benzoic acid from cranberry juice.

To screen the suitable membranes for separation of benzoic acid from cranberry juice, fifteen kinds of commercial nanofiltration membranes from six different manufacturers, made from different materials were investigated with bench scale system (dead-end test cell) of nanofiltration. Result indicates that rejection of benzoic acid was significantly lower than that of other components in cranberry juice, including: anthocyanins, sugars, organic acids. The permeate fluxes of membranes were significantly different, even when the pore sizes of membranes were the same. The 7 promising membranes for benzoic acid separation from cranberry juice were HC50, NFT50, G5, Desal-DK, DRA4510, UTC60 and NTR7250 because they exhibited the large difference in rejection of benzoic acid (approximately or higher 40%) and other components in cranberry juice, and the high rejection against sugars and organic acids (above 70%).

Six kinds of commercial nanofiltration membranes, including NFT50, G5, Desal-DK, DRA4510, UTC60 and NTR7250, were investigated into the effects of the operative conditions in cross flow plate and frame system. Results showed that, rejection of benzoic acid was significantly lower than that of other components in cranberry juice, including sugars and other organic acids. In range of 2 - 7.5 L/min, feed flow rate slightly affected on the performance of nanofiltration. The higher temperature resulted in higher permeate flux and lower rejection of benzoic acid, whereas rejection of sugar and organic acid was stable at high value. In range of 2.5 – 5.5, pH also significantly affected on separation of benzoic acid and negative rejection against benzoic acid was observed at pH 4.5 with some kinds of membranes. It implies that pH 4.5 is considered as optimum pH for benzoic acid separation from cranberry juice. The

lower permeate flux caused lower rejection of benzoic acid and negative rejection of benzoic acid was observed at low permeate flux. The pretreatment by ultrafiltration with CR61PP membrane could improve the permeate flux but insignificantly influenced on the efficiency of separation. The results also indicated that NFT50 and DK membranes can be effectively used to separate benzoic acid from cranberry juice.

Then, the nanofiltration of cranberry juice in plate and frame pilot system was investigated was carried out with NFT50 membrane at pH 2.5 (natural pH of cranberry juice) and pH 4.5 (optimum pH for benzoic acid separation) with concentration mode. In case of cranberry juice at pH 2.5, nanofiltration rejected above 70% of benzoic acid and approximately remained 95%, 86% and 97% of total soluble solid (based on Brix), total organic acids and sugars, respectively, at 4.23 of concentration factor. With cranberry juice at pH 4.5, nanofiltration rejected more than 80% of benzoic acid and approximately remained 92%, 91% and 94% of total soluble solid (based on Brix), total organic acids and sugars, respectively, at 2.89 of concentration factor. Effectiveness of cleaning procedure was investigated and the result showed that the cleaning with Ultrasil 10 (0.25 %w/v) could recover more than 90% of pure water permeability.

To know the rejection of individual components, nanofiltration of pure solution of glucose, citric acid, malic acid and benzoic acid with concentration being same with themselves in cranberry juice with NFT50 membrane and Desal DK membrane were investigated in ranges of 2.5 – 5.5 of pH. Result indicated that rejection of benzoic acid and malic acid was strongly affected by pH, whereas that of glucose and citric acid was high and stable.

The modeling of nanofiltration to separate benzoic acid from cranberry juice was investigated to estimate membrane area and characteristics of nanofiltration in practical scale. The simulating result of nanofiltration at pH 4.5 (recovering benzoic acid) showed that the NFT50 membrane area requiring for nanofiltration of 1000 L of cranberry juice at 3 MPa in 6 hours to recover 90% benzoic acid was 10.023 m^2. And 573.3 L of permeate containing approximately 155 ppm of benzoic acid was obtained. On the other hand, for nanofiltration at pH 2.5(concentration simultaneously with recovering benzoic acid), in order to process 1,000 L of cranberry juice, that requires 9.83 m^2 of NFT50 membrane area for nanofiltration at 4 MPa in 140 min to obtain 3.0 of concentration factor. Recovery yield of glucose, citric acid and malic acid were 0.96, 0.92 and 0.47, respectively. While, 73% of benzoic acid was rejected from feed and the concentration of benzoic acid in the permeate was approximately 100 ppm.

The second nanofiltration of permeate from the first nanofiltration for purification of benzoic acid was also investigated with NFT50 membrane and model solutions at pH 4.5. The result indicates that benzoic acid content in permeate of second nanofiltration was about 10 % higher than that in feed, whereas the concentration of sugars and organic acids strongly reduced and became significantly low (lower than 0.1%w/v of glucose and citric acid and about 0.12 %w/v of malic acid). To recover 90% benzoic acid in 1,000 L of feed from permeate of the first nanofiltration at pH 4.5, it requires 5.4 m^2 of membrane area to process in 210 min at 2 MPa of operating pressure. Concentration of benzoic acid in permeate was approximately 175 ppm. If feed stock was permeate from the first nanofiltration at pH 2.5, it also requires 5.4 m^2 of membrane area to process 1,000 L in 120 min at 3 MPa of operating pressure. Concentration of benzoic acid in permeate was approximately 110 ppm.

In conclusion, my research on nanofiltration of separating benzoic acid from cranberry juice indicated that it is promising to recover benzoic acid from cranberry juice. On technical side, it is feasible to build up an industrial scale plant for recovering benzoic acid from cranberry juice and use as a natural preservative. However, the economic assessment is required to ensure profitability of the process. Moreover, result obtained from this research is also useful to extend for study on recovering benzoic acid from the cranberry cake that is a byproduct of cranberry juice processing.

学位論文審査の要旨

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学位論文題名

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本論文は、図38、表18、引用文献114編からなる総頁161頁の英文論文であり、他に参考論文1編が添えられている。

ナノろ過（Nanofiltration, NF）は圧力駆動型の膜ろ過・分離技術であり、分離可能分子サイズを指標とすると、限外ろ過（Ultrafiltration, UF）と逆浸透圧（Reverse osmosis, RO）の中間に位置づけられる。その主な分離メカニズムは篩別効果と電気的排除機能にあるとされている。今日のナノろ過は低温度下で操作が可能であり、対象材料（食品）の固有性質に悪影響を及ぼさず、かつエネルギー消費量が少ないなどの特徴を有すことから、食品産業では幅広く応用されている技術である。加えてナノろ過装置は構造が単純なため設置が容易で、操作および維持管理もし易い点などが実用上の利点として挙げられている。特に近年の省エネルギー、温室効果ガス発生抑制の流れの下で、低投入型・環境配慮型分離技術の代表ともされている。

一方、安息香酸（C_6H_5COOH, Mw=122）は保存料として国際的にも認可されており、食品や化粧品によく使用されている。通常、安息香酸は石油由来のトルエン（$C_6H_5CH_3$）を酸化することで製造され、その製造プロセスはエネルギー消費量が大きく、また製品の純度も低いことから精製などの付加的プロセスを要す場合もあり、結果的に製造コストが高くつくといわれている。

以上のことから、本論文では、北米からわが国に輸入されるクランベリー（cranberry, *Vaccinium macrocarpon*）ジュースが安息香酸を比較的高濃度（178ppm）に含有するので、これを原料とするナノろ過による安息香酸回収を幾つかの市販ろ過膜を用いた実験とモデリングによって検証し、低コストかつ環境配慮型（非石油由来）安息香酸抽出技術の開発に資することを目的とした。

1）15種類の市販ナノろ過膜を準備し、実験室規模のナノろ過装置（dead-end test cell）に供試し、バッチ運転にてそれらの分離性能を調査した。原料（濃縮：Brix濃度50度）のクランベリージュースはBrix濃度で10度に調整され、さらに限外ろ過膜GR61PP（DDS, MWCO:20,000Da）にて前処理をした後にナノろ過に供された。実験の結果、膜の製造メーカ、材質、型式（目標性能）によってそれらの性能は様々であったが、透過液中の目標物質（安息香酸）濃度とその他の

成分（アントシアニン、糖類、有機酸）、および排除側のそれら濃度、さらに透過流量を指標に判定した結果、HC50、NFT50、G5、Desal-DK、DRA4510、UTC60、NTR7250が良好な成績を出した。全体を通じてpH=4.5に調整した場合が、pH=2.5、pH=3.5の場合よりも排除特性が良好であった。

2）上記で比較的良好な性能を示した7種類からHC50を除く6種類を6連式連続ろ過装置に組み込んで最適膜の絞り込みを行った。ここでは、透過液および排除液を再び混合して繰り返し使用した。また、限外ろ過による前処理の有無の2区分、および送液圧力を2～4MPa、速度を2～7.5L/min、原料pHを2.5～5.5の範囲で変化させた。評価指標は上記1）の場合と同様である。実験結果は、限外ろ過による前処理がナノろ過の性能を向上させること、またpH=4.5にて最適となることを示し、NFT50とDesal-DKの2種がクランベリージュースからの安息香酸分離に向いていることが分かった。

3）選択されたNFT50およびDesal-DKを用いて実際のクランベリージュースのpH=2.5とこれをpH=4.5に調整した場合とを比較検証した。pH=2.5では安息香酸の分離（回収）能力は約70%であったが、pH=4.5では約80%へと向上した。また他の成分の排除もより効率的であった。特に安息香酸とリンゴ酸がpH=4.5において際立っていた。これは、上述したナノろ過の特徴的分離メカニズムに起因するものと考えられた。また、連続運転中は適宜に膜洗浄工程を挿入することによって分離能力をより長時間にわたって維持できることも確かめられた。

4）2種類の実験結果を基に動力学的モデルのパラメータ推定を行い、それらによる試算の結果、NFT50の膜を用いる場合、pH=4.5、1,000Lのクランベリージュースを圧力3MPaで運転し、6時間で90%の安息香酸回収を行うには、約10m^{2}の有効膜面積が必要であることなどを明らかにした。

以上のように、本論文では、クランベリージュースからナノろ過によって安息香酸を回収する実験とモデル試算とからナノろ過が有効であり、時代の趨勢に合致する低コストかつ環境配慮型（非石油由来）安息香酸抽出技術としての要件を満たすものであることを明らかにした。またクランベリージュースの場合はpH=4.5が適正pH条件であり、限外ろ過による前処理、さらに定期的膜洗浄の挿入によって回収効率の改善と長時間運転を可能にするなどの実用運転に資する情報も提供しており評価できる。

よって、審査員一同は、Lai Quoc Datが博士（農学）の学位を受けるのに十分な資格を有するものと認めた。