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Nanofiltration process for the nutritional enrichment and refining of rice bran oil

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ABSTRACT

Crude rice bran is a natural source of γ-oryzanol, a nutritionally valuable phytochemical with antioxidant properties. In the present paper the refining and γ-oryzanol enrichment of rice bran oil was investigated through solvent extraction optimization and nanofiltration processing. Several solvent resistant nanofiltration membranes were screened and successfully applied in a two step membrane cascade with fluxes between 39 and 53 L m^{-2} h^{-1}. A first membrane stage operation provided the separation between glycerides and γ-oryzanol, promoting the oil enrichment in this phytochemical. In the second membrane stage the oil could be refined to acceptable consumption levels (FFA < 0.20 wt.%) and its γ-oryzanol content was further enhanced. Overall, the integrated process provided a RBO γ-oryzanol enrichment from 0.95 to 4.1 wt.% in oil, which corresponded to more than a two fold increase in the oil's antioxidant capacity. These results demonstrate the potential of organic solvent nanofiltration as a technology to enrich and refine oil based products.

1. Introduction

Crude rice bran (CRB), a by-product of rice milling, is rich in phytochemicals of high nutritional value, such as γ-oryzanol, tocopherols and tocotrienols. γ-Oryzanol consists of a mixture of ester compounds derived from the reaction of trans-ferulic acids with phytosterols and triterpene alcohols (Lerma-Garcia et al., 2009). γ-Oryzanol has natural antioxidant properties and has also been shown to have remarkable cholesterol reducing properties (Sugano and Tsuji, 1997; Xu et al., 2001). Commercial rice bran oil (RBO) is obtained from CRB through a process involving two major operations: (i) solvent extraction of CRB to obtain RBO and subsequent solvent distillation, and (ii) refining of the obtained RBO. The solvent extraction is typically done by using hexane due to its extraction power and low boiling point. After removing hexane by distillation, the oil is refined using caustic chemicals (e.g. sodium hydroxide solution) to neutralize free-fatty acids (FFA) and phospholipids, and remove them by forming a solid soapstock. The RBO is then submitted to bleaching, de-waxing and deodorizing. It is reported that 90% of γ-oryzanol is lost during the refining process, from its original value of 1–1.4% in crude RBO to less than 0.15% in a commercial chemically refined RBO (Krishna et al., 2001, 2006; Van Hoed et al., 2006). In view of γ-oryzanol's beneficial properties, there is considerable interest in developing RBO refining processes that are able to maintain or enrich the γ-oryzanol content in RBO.

Current state-of-the-art technologies for RBO nutritional enrichment involve the use of either distillation technology (short-path or conventional distillation), or preparative liquid chromatography. These technologies require high capital expenditure to set up and have significant operating costs due to their productivity limitations and solvent consumption (Lai et al., 2005). In recent years, sub- and super-critical fluids such as carbon dioxide and liquefied hydrocarbons have become popular in lab-scale preparation of natural oils, as they provide considerably lower toxicity than conventional solvents and are easily separated from the extracts (Xu and Godber, 2000). In particular, Balachandran et al. (2008) presented an integrated super-critical carbon dioxide approach to extract and refine RBO, in an attempt to preserve the phytochemical levels in the final RBO. The reported oil yields were similar to the ones obtained with conventional hexane extraction, but the final γ-oryzanol concentration was only between 0.6 and 1.2 wt.%. In addition, the high operating pressures required, and compaction/channelling problems associated with large-scale extraction, reduce the feasibility of employing this technique on an industrial scale. The high capital costs involved in implementing such technology also deters industrial interest, which generally favour more economical plug-in technologies.

Recently, membrane technology, particularly organic solvent nanofiltration (OSN), has attracted attention as an alternative molecular separation technology (Nasso and Livingston, 2008). The main advantage of employing OSN for purification of natural

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extracts is that by selecting suitable molecular weight cut-off (MWCO) membranes, this technology can be used to fractionate molecules of similar molecular weight (e.g. in the 200–1000 Da range; Sereewatthanawut et al., 2010). One of the key problems of processing natural compounds is that they are often susceptible to thermal damage, and thus the mild (near-ambient) operating conditions of membrane processes can minimise nutritional losses due to thermal degradation. Manjula and Subramanian (2008) have reported the application of a membrane-based process for the enrichment of γ-oryzanol in RBO, though without addressing oil refining. In their study, batch-mode, dead-end filtration experiments were conducted with undiluted RBO and hexane-diluted RBO systems. Despite up to 1.55-fold enrichment being obtained with undiluted RBO, the permeate fluxes obtained (less than 0.03 $L\,m^{-2}\,h^{-1}$) were too low to provide a viable industrial process. Flux improvement was observed when hexane-diluted RBO was filtered, but this was at the expense of enrichment fold and process yield, which also compromises the feasibility of operating such process at industrial scale.

The main objective of the present investigation was to explore the potential application of OSN, as a plug-in technology in the conventional RBO production process, to refine crude RBO and create a γ-oryzanol-enriched product. This novel approach could potentially allow RBO refining with minimal loss of phytochemicals, and eventually, also allow solvent recycle back into the extraction process. The secondary objective was to verify that the enriched product oil contained substantially more antioxidant capacity than the crude RBO.

2. Materials and methods

2.1. Materials and chemicals

CRB supplied by Bunge Oil, Inc., USA was stored below 5 °C and used without any further treatment. γ-Oryzanol powder of ⩾98% purity was obtained from Tsuno Rice Fine Chemical Co. Ltd., Japan. All chemicals used were HPLC grade and purchased from Sigma–Aldrich, UK. Membranes used in this study were commercial integrally skinned asymmetric membranes of the Starmem™ and DuraMem™ membrane series (supplied by Evonik Membrane Extraction Technology, Ltd. (MET), UK), and developmental membranes also provided by MET.

2.2. γ-Oryzanol solubility

The γ-oryzanol solubility was determined in hexane, ethyl acetate, acetone, i-propanol and water. Known amounts of γ-oryzanol were added into a fixed volume of each of the solvents tested until saturation was reached. The vials were left to mix at 20 °C for a period of 24 h. A known volume of each saturated solution was evaporated under nitrogen and the deposit re-dissolved in a known (larger) volume of ethyl acetate. After appropriately dilution, the samples were analysed by HPLC as described below and the solubility concentrations determined using a calibration curve. The values presented were an average of three measurements and the variability was ±3%.

2.3. Solvent extraction

A known amount of rice bran was extracted with different solvents including hexane, ethyl acetate, acetone, i-propanol and water for a certain period (from 0.5 to 24 h). The solids were then removed by filtration using a Whatman no. 2 filter paper under vacuum and the purified extract was then used for membrane processing. Part of this extract was also evaporated at low pressure to determine the dry weight of the extract (i.e. oil). The oil extraction yield was calculated as follows:

$$\text{Yield}\,(\%) = \frac{\text{Extract dry weight}}{\text{Mass of crude rice bran}} \times 100 \quad (1)$$

The extracted oil was then further analysed for γ-oryzanol and FFA content. Since glycerides are the major component in RBO, components apart from γ-oryzanol and FFA are henceforth defined as glycerides for simplicity. The oil yields presented were an average of three measurements and the standard deviation was below 1 wt.%. The γ-oryzanol content in the oil presented was an average of three measurements and standard deviation was below 0.6 wt.%.

2.4. Analytical methods

γ-Oryzanol concentration was determined by reverse-phase HPLC (Agilent 1100 series) using an ACE-C18 column (250 × 4.6 mm) packed with 5 μm diameter silica particles with 300 Å pores size. Prior to HPLC analysis all samples were evaporated under nitrogen and re-dissolved in ethyl acetate. A calibration of γ-oryzanol in ethyl acetate was prepared to determine the γ-oryzanol concentrations in the samples. The analysis was performed according to the method described by Xu and Godber (1999), using as mobile phase a mixture of methanol, acetonitrile, dichloromethane and acetic acid (50:44:3:3) and a flow rate of $1\,mL\,min^{-1}$. A UV–vis detector was used with a wavelength set at 330 nm. The FFA content was determined by standard titration with KOH according to the AOCS Official method Ca 5a-40 (1997), whilst the glycerides content of the oil was determined by subtracting the γ-oryzanol mass and the FFA mass from the total sample dry-weight.

2.5. Membrane cross flow filtration – membrane screening

Membrane filtration experiments were conducted using a METcell crossflow filtration apparatus (MET Ltd., UK). The METcell apparatus consisted of an 800 mL capacity feed vessel and a pumped recirculation loop through two to five crossflow cells connected in series. The crossflow system is shown schematically in Fig. 1 for a system containing four crossflow cells. Mixing in the crossflow cells was provided by flow from the gear pump – the flow is introduced tangentially to the membrane surface at the outer diameter of the membrane disc and follows a spiral flow pattern to a discharge point at the centre of the filtration cell/disc. Nanofiltration membrane discs with an effective area of 14 cm^2 were conditioned with process solvent at the operating pressure and temperature (30 °C) until a constant flux was obtained, to ensure that any preservatives/conditioning agents were washed out of the membrane, and that maximum compaction of the membrane was achieved at the operating pressure. This step generally took 1 h. The solution mixture was then permeated across each conditioned membrane disc at specified operating pressures (5–30 bar). When the permeate was not being sampled, the permeate streams from each filtration cell were collected and fed back to the feed tank by HPLC pump – this maintains constant volume and operating conditions in the system. Samples of feed, permeate and retentate fractions were collected every 30 min for analysis.

2.6. Membrane characterization

Two parameters were used to characterize the membrane performance in this study, permeate flux and solute rejection. Permeate flux ($L\,m^{-2}\,h^{-1}$, LMH) was obtained by measuring the volume permeated through the membrane per unit area per unit time using the following equation: