Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Membrane Science 276 (2006) 23–30
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Recovery of caprine milk oligosaccharides with ceramic membranes

Antonio Martinez-Ferez *, Antonio Guadix, Emilia M. Guadix

Department of Chemical Engineering, Campus Fuentenueva s/n, University of Granada, 18071 Granada, Spain

Received 24 May 2005; received in revised form 2 September 2005; accepted 12 September 2005
Available online 10 October 2005

Abstract

Caprine milk contains a large amount of different sialylated and neutral lactose-derived oligosaccharides compared to cow or sheep milk. In addition, its oligosaccharide profile is very similar to human milk, which suggests it has similar physiological activity. Thus, the caprine milk oligosaccharide fraction is a very promising food ingredient for human nutrition applications, especially for the supplementation of infant formulas. In this research work, a two-step cross-flow filtration process was designed in order to recover the caprine milk oligosaccharides. Tubular ceramic membranes with molecular weight cut-offs of 50 and 1 kDa, respectively, were employed in two separated, consecutive continuous diafiltration steps, in which the cumulated permeate from the first step was the initial feed in the second one. A final retentate containing more than 80% of the original oligosaccharides and less than 4% of the original lactose and protein was obtained.

Keywords: Caprine milk; Oligosaccharides; Ceramic membranes; Infant nutrition

1. Introduction

The glucidic fraction of milk contains, along with lactose (the major carbohydrate), nucleotide sugars, glycolipids, glycoproteins, and oligosaccharides [1]. In particular, human milk is considered to be unique with regard to its high content and singular proportion of complex fucosylated and sialylated lactose-derived oligosaccharides [2]. Although in most cases their structure and/or functions are not yet fully understood, some of these biomolecules are discussed as being involved in the infant's defence system, the development of a specific intestinal microflora and in inflammatory processes [3]. Besides these properties, some researchers suggest that human milk contains a significantly higher concentration of exogenous sialic acid, than bovine milk or any type of infant formula [4]. In this sense, sialic acid has been demonstrated to participate as an integral part of ganglioside structure in synaptogenesis and neural transmission [5], contributing to the differences in neurodevelopment between breastfed and bottle-fed infants [4].

Caprine milk has recently been reported to contain a large amount of different sialylated and neutral lactose-derived oligosaccharides compared to cow or sheep milk, which is very similar to the oligosaccharide profile in human milk [6]. The caprine milk oligosaccharides seem to inhibit the monocyte adhesion to human umbilical vein endothelial cells, which suggest they may act as anti-inflammatory agent in the newborn infant [7]. Thus, based on these findings, caprine milk oligosaccharides are a very promising functional food ingredient for human nutrition applications, especially for the supplementation of infant formulas.

Within membrane technology, ultrafiltration and nanofiltration processes have proven to be an efficient way in the separation of carbohydrates. Aydogan et al. [8] studied the effect of feed flow rate, operating pressure, and feed concentration on the separation of glucose and sucrose with 500 Da nanofiltration membranes. With respect to oligosaccharides, Goulas et al. [9] demonstrated the potential of cross-flow nanofiltration in the purification of a galacto-oligosaccharide syrup containing contaminants monosaccharides by using cellulose acetate and thin film composite membranes. Goulas et al. [10] developed a process for the production of isomaltooligosaccharides (degree of polymerisation greater than 5) from sucrose in a recycle enzyme reactor coupled with a 10 kDa polyethersulfone/polysulfone membrane.

On the other hand, membranes have been employed in the extraction of valuable bioactive compounds from milk. For instance, Lal Baruah et al. [11] recovered human IgG fusion protein from transgenic caprine milk employing 0.1 μm tubu-

* Corresponding author. Tel.: +34 958243314; fax: +34 958248992.
E-mail address: amferez@ugr.es (A. Martinez-Ferez).

0376-7388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2005.09.027

lar hollow fiber polyethersulfone membranes. Ulber et al. [12] designed a downstream process to recover bovine lactoferrin from sweet whey and evaluated the performance of organic (tubular, spiral, and flat-sheet) and ceramic membranes to this end. Furthermore, hybrid membrane processes like the one described by Sarney et al. [13], based on a combination of enzymatic treatment and nanofiltration, have proven its effectiveness for the isolation of oligosaccharides from human milk.

In this research work, we describe a two-step cross-flow ultrafiltration–nanofiltration process employing tubular ceramic membranes which allows to recover more than 80% of the original caprine milk oligosaccharide fraction. This type of sequential strategy has shown good results in the fractionation of whey proteins [14]. In the first step, starting from skim caprine milk, a 50 kDa membrane preferently retains the proteins, while the oligosaccharides and lactose are collected in the permeate. In the second step, lactose is eluted in the filtrate employing a 1 kDa membrane and the oligosaccharides are finally obtained in the retentate.

2. Experimental

2.1. Materials

The milk used in this study, supplied by Puleva Biotech (Granada, Spain), was pasteurised skim caprine milk from the Murciano-Granadina breed. Before pasteurisation, milk was filtered in order to remove any gross contaminant.

The membranes were multichannel tubular ceramic INSIDE CéRAM^{TM} modules (TAMI Industries, Lyon, France) made of ZrO_2–TiO_2, 25 cm long, with three channels, and a membrane area of 94 cm^2.

2.2. Experimental rig

The experimental rig (Fig. 1) consisted of a 2 L feed tank immersed in a thermostatic bath at 30 °C, a precision positive displacement recirculation pump (Procon, TN, USA), a filtration housing, one back-pressure valve and manometers, a flowmeter (Iberfluid, Barcelona, Spain), and two tanks for permeate collection and buffer supply.

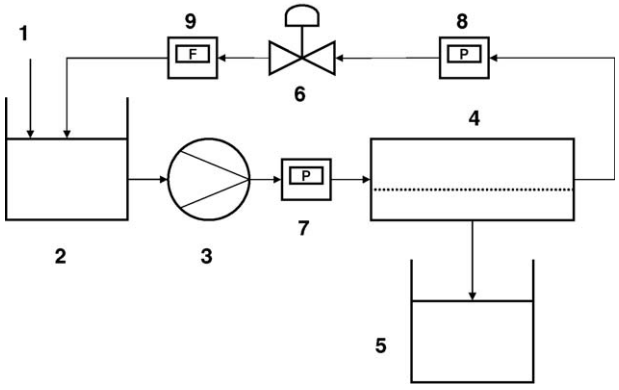

Fig. 1. Drawing of the experimental system. (1) Diafiltration water supply, (2) feed tank, (3) recirculation pump, (4) membrane module, (5) permeate tank, (6) back-pressure valve, (7) manometer, (8) manometer, and (9) flowmeter.

2.3. Filtration process

A two-step cross-flow filtration process was selected. The mode of operation consisted of two separated, consecutive continuous diafiltration steps. The molecular weight cut-offs selected were 50 kDa for the first step and 1 kDa for the second one. Skim caprine milk was employed as initial feed in the first step. The cumulated permeate from the first step was collected and employed as initial feed in the second one.

2.3.1. First step

The objective of this step was to retain the protein fraction while obtaining the oligosaccharides and lactose in the permeate (Fig. 2a).

Prior to use, the 50 kDa membrane was conditioned by flushing with demineralised water at 30 °C for 30 min to hydrate the membrane material and remove possible contaminants. Clean membrane resistance was determined by measuring water flux at 30 °C. Transmembrane pressures were set in the 0–250 kPa range and cross-flow velocity was set at 3.3 m/s. Then, skim caprine milk at 30 °C was filtered, recycling both retentate and permeate. Initial permeate flux measurements were taken for 1 min at different transmembrane pressures values up to 250 kPa at a cross-flow velocity of 3.3 m/s.

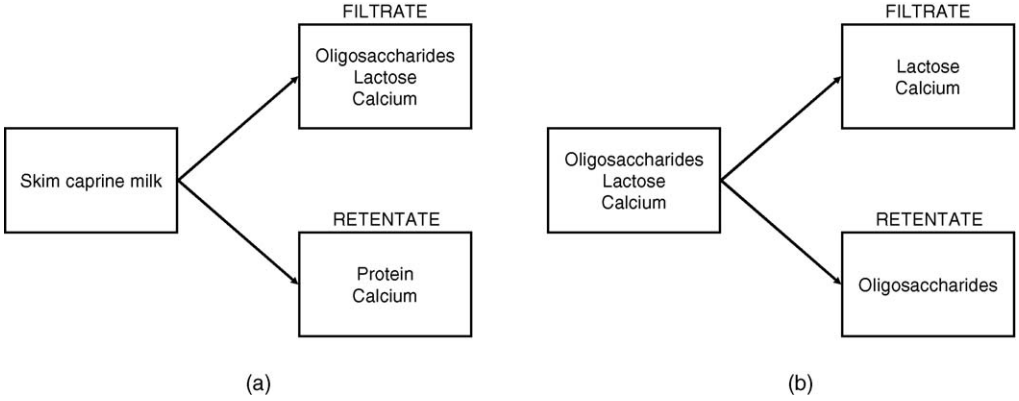

Fig. 2. Scheme of the separation process. (a) First step (50 kDa) and (b) second step (1 kDa).