Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Changes in structure and performance during diafiltration of binary protein solutions due to repeated cycles of fouling/alkaline cleaning

M. Carmen Almécija[a], Antonio Guadix[a], José I. Calvo[b,*], Emilia M. Guadix[a]

[a] Department of Chemical Engineering, University of Granada, 18071 Granada, Spain
[b] SMAP (Group of Surfaces and Porous Materials), Department of Applied Physics, University of Valladolid, 34071 Palencia, Spain

ARTICLE INFO

Article history:
Received 1 March 2017
Received in revised form 20 June 2017
Accepted 7 July 2017
Available online 17 July 2017

Keywords:
Ceramic membrane
Chemical cleaning
Fouling
Liquid–liquid displacement porosimetry
Protein fractionation
Protein retention

ABSTRACT

The purpose of this work was to evaluate the effect of the temperature (50 and 60 °C) of a NaOH cleaning solution during the diafiltration of a binary mixture of bovine serum albumin and β-lactoglobulin, through a 300 kDa tubular ceramic membrane along repeated operational cycles. To this aim, final permeate volume, membrane and fouling resistances and individual protein concentration were analyzed. At the end of each individual study, the membranes were characterized by liquid–liquid displacement porosimetry. As a result, 50 °C was found to be the most appropriated temperature due to its higher capability to restore the initial membrane resistance and the higher efficiency achieved in terms of protein separation. Both conditions fulfilled without altering the structural properties of the membrane as given by porosimetric analysis. In contrast, a great fouling resistance involving null protein transmission occurred when cleaning was performed at 60 °C.

1. Introduction

In the last years, extensive research has been focused on the separation and purification of proteins by membrane technology (van Reis and Zydney, 2007). In particular ultrafiltration (UF), has found a widespread application in the concentration and desalting of proteins (Ghosh, 2003). This process is able to achieve high productivity and concentrate purity simultaneously (Saksena and Zydney, 1994; Ghosh et al., 1998). Moreover, selectivity towards individual proteins in a complex mixture (a usual drawback when ultra-filtering non model proteins) can be enhanced through the application of high performance tangential flow filtration (HPTFF), where a proper choice of pH and ionic strength maximizes differences in the effective hydrodynamic volume of the different proteins (van Reis et al., 1997; Almeícija et al., 2007).

However, membrane operation (not only UF) is generally characterized by a progressive decrease in permeate flow and protein transmission along the time (Chan and Chen, 2004), which diminishes the strong potential of membranes as a choice separation method for the biotechnological processes. Very often the proteins or other solutes filtered or retained in the membrane lead to adhesion onto the membrane surface, directly or forming aggregates. This phenomenon, mostly irreversible and usually termed as membrane fouling, causes a progressive and substantial decrease of membrane performance characteristics with time. In any case, fouling is usually reverted by periodic chemical and physical cleaning, which ideally intends to restore the original filtration characteristics of the virgin membrane (D'Souza and Mawson, 2005). That cleaning increases the membrane lifetime, a critical factor due to the considerable costs rise associated to membrane replacement.

Membranes in industry are regularly maintained and cleaned in place (CIP), a practice comprising several steps as: (i) emptying the filtration system from both sides of the membrane, usually followed by backflushing; (ii) chemical cleaning after addition of several

* Corresponding author.
E-mail addresses: mcalmeci@ugr.es (M.C. Almécija), jicalvo@termo.uva.es (J.I. Calvo).
http://dx.doi.org/10.1016/j.fbp.2017.07.003

cleaning agents, and; (iii), disinfection and final water rinsing, especially in biotechnological, food or pharmaceutical industries (Shi et al., 2014). For those later industries, even sterilization should be required in most cases.

Therefore, from a practical point of view, the operation of membrane plants takes place in a cyclic mode including filtration and cleaning steps. In the case of proteins, NaOH solutions are mentioned in the literature for their capability of removing protein deposits, which is improved with the concomitant action of a surfactant (Cheryan, 1998).

Although a considerable amount of research has addressed the problem of membrane cleaning optimization (Weis et al., 2005; Alzahrani et al., 2013), studies of membrane cleaning have always been a complementary aspect, paying much more attention to a deeper knowledge of fouling. Only a few quantitative works have been published studying the effect of repeated fouling and cleaning cycles on the performance of ultrafiltration membranes (Blanpain-Avet et al., 2004; Popović et al., 2009; Ebrahim, 1994).

For example, Weis and Bird (2001) and Weis et al. (2005, 2003) studied the influence of fouling and cleaning processes over a number of operational cycles upon polymeric (polyethersulphone, polysulphone and regenerated cellulose) UF membranes fouled with products related to the pulp and paper industries, using formulated cleaning agent (P3 Ultrasil 11), sodium hydroxide or nitric acid as chemicals. Authors concluded that over long term operation, as the membrane surface became irreversibly fouled, physico-chemical interactions between cleaning agent and foulant were the dominant factors in determining the cleaning performance while membrane material, including its porosity and surface roughness, was less determining.

Blanpain-Avet et al. (2004) investigated the effect of 10 repeated fouling and cleaning cycles upon the membrane and cleaning performance of a 0.1 μm tubular ceramic microfiltration (MF) membrane with a whey protein concentrate as foulant. Their results showed that sodium hydroxide recovered flux whereas nitric acid had a negative effect on membrane resistance. They also found a slight increase on protein retention over the last few cycles indicating a change in membrane selectivity, although the cleaning efficiency did not decrease with cycles.

Mourouzidis-Mourouzis and Karabelas (2006, 2008) studied the fouling of MF ceramic membranes employed in successive whey protein filtration cycles with intermediate backwashing. Their results indicated that irreversible fouling occurred mostly during the first cycle and did not significantly increased later on whereas reversible fouling developed in each cycle, mainly during the first minutes of filtration.

Zapata-Montoya et al. (2006) studied the evolution of permeate flux, transmission of protein and membrane resistances, for a 50 kDa tubular ceramic membrane, along 50 cycles comprising milk ultrafiltration, alkaline and acid cleaning. Permeate fluxes and protein transmission did not suffer significant changes during the cycles. However, membrane resistance increased, mainly in the first operational cycles, which suggests the formation to some extent of a "chemically" irreversible fouling. Finally alkaline cleaning was able to reduce membrane resistance in one order of magnitude respect to that obtained just after finishing ultrafiltration, whereas acid cleaning decreased only 10% the membrane resistance value after alkaline cleaning.

According to the referred literature, it is worth to study the variables involved in the cleaning procedure of the operational cycles in order to detect any adverse effects caused by the cleaning agents on the expected membrane working lifetime (Wagner, 2001; Lawrence et al., 1998). In particular, temperature is a critical variable because of its narrow margin of effective use, which results in poor cleaning performance at low temperature values and corrosive action at high ones.

Generally, an elevated temperature results in better membrane cleaning. However, it must keep in mind possible risks for membrane material stability and the increase of attraction between foulant layers which leads to stronger attachment to membrane surface and consequently more difficult to breakup (Shi et al., 2014).

In any case, the efficiency of the cleaning step should lead to detectable changes in the membrane structure along time, due to deposition of subsequent fouling layers and corresponding reduction on the membrane mean pore size and pore size distribution (PSD). These changes can be detected with the aid of porosimetric techniques through an autopsy of the used membrane after a gentle number of fouling/cleaning cycles.

The purpose of this research work was to study the effect of the temperature of the alkaline solution employed as cleaning agent in repeated cross-flow filtration and cleaning stages. Two temperatures were chosen for this study (50 °C and 60 °C), both in the range of temperatures often used to clean membranes after protein UF. In the preliminary work of this research, a wider range of temperatures was assayed in our laboratory. Nevertheless, these experiments were not included in the manuscript since, after a short number of cycles they conducted to improper results. For temperatures below 50 °C, membrane cleaning was not effective at all. On the other hand, for temperatures above 70 °C, membrane erosion was very noticeable.

2. Experimental

Two main factors (permeability and selectivity) are to be considered to check the success of a certain membrane for some industrial process. In that sense, present study will start accounting for possible changes in flux along time, due to an increase of fouling resistance. Attending to selectivity, protein transmissions were monitored during the diafiltration of a protein binary solution made of bovine serum albumin and β-lactoglobulin through a tubular ceramic membrane with molecular weight cut off (MWCO) of 300 kDa. Moreover, membrane and fouling resistances were measured after each stage during the operational cycles. Finally, at the end of each protocol, the membrane PSD was characterized by liquid–liquid displacement porosimetry (LLDP) to check possible changes in membrane structure. LLDP has proven to be reliable on characterizing from structural point of view membranes in the UF range (Carretero et al., 2013), but also the information it provides can be used to estimate functional performance related parameters, as permeability or MWCO (Calvo et al., 2011).

2.1. *Materials*

As a filtration solution, it was employed a binary mixture of bovine serum albumin (BSA) and β-lactoglobulin (BLG), both with reagent purity and received from Sigma-Aldrich (St. Louis MO, USA). Selection of the proteins in this study was because both are different enough (respective molecular weights of 18.4 kDa for b-lactoglobulin and 66.5 kDa for BSA) to be effectively separated in appropriated conditions of filtration.

Protein solutions were prepared at a concentration of 0.125 g/L on each protein. Solution pH was adjusted to 5 by addition of appropriated amounts from a 37% concentrated solutions of HCl. At such value, very close to the IEP of both proteins (4.9 for BSA and 5.2 for BLG), it was found maximum selectivity for BLG (Ibañez, 2007).

The membrane selected was a tubular ceramic Céram Inside module (TAMI Industries, Lyon, France) made of ZrO_2–TiO_2, 25 cm long and with a filtration area of 47 cm^2. The nominal molecular weight cut-off of the membrane was 300 kDa, which was found previously to allow the transmission of significant amounts of β-lactoglobulin (18.4 kDa) while retaining most of the bovine serum albumin (66.5 kDa) (Ibañez, 2007).

Three membranes were used in this study: two of them, A and B, served to 30 operational cycles with alkaline cleaning at 50 °C and 60 °C, respectively, while an extra membrane served as control.

In a previous paper by some of the authors (Guadix et al., 2010), milk was filtered with a 50 kDa ceramic membrane for 50