J. Dairy Sci. 97:1–13
http://dx.doi.org/10.3168/jds.2014-7957

A physicochemical investigation of membrane fouling in cold microfiltration of skim milk

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ABSTRACT

The main challenge in microfiltration (MF) is membrane fouling, which leads to a significant decline in permeate flux and a change in membrane selectivity over time. This work aims to elucidate the mechanisms of membrane fouling in cold MF of skim milk by identifying and quantifying the proteins and minerals involved in external and internal membrane fouling. Microfiltration was conducted using a 1.4-μm ceramic membrane, at a temperature of 6 ± 1°C, cross-flow velocity of 6 m/s, and transmembrane pressure of 159 kPa, for 90 min. Internal and external foulants were extracted from a ceramic membrane both after a brief contact between the membrane and skim milk, to evaluate instantaneous adsorption of foulants, and after MF. Four foulant streams were collected: weakly attached external foulants, weakly attached internal foulants, strongly attached external foulants, and strongly attached internal foulants. Liquid chromatography coupled with tandem mass spectrometry analysis showed that all major milk proteins were present in all foulant streams. Proteins did appear to be the major cause of membrane fouling. Proteomics analysis of the foulants indicated elevated levels of serum proteins as compared with milk in the foulant fractions collected from the adsorption study. Caseins were preferentially introduced into the fouling layer during MF, when transmembrane pressure was applied, as confirmed both by proteomics and mineral analyses. The knowledge generated in this study advances the understanding of fouling mechanisms in cold MF of skim milk and can be used to identify solutions for minimizing membrane fouling and increasing the efficiency of milk MF.

Key words: membrane fouling, cold microfiltration, protein fouling

INTRODUCTION

Microfiltration (**MF**) has gained significant attention in recent years as a processing method for the removal of microorganisms from milk. Microfiltration of milk using large-pore-size membranes has been shown to be very efficient in removal of bacteria, spores, and somatic cells from skim milk, while allowing almost complete permeation of other milk components (Saboya and Maubois, 2000; Te Giffel and Van der Horst, 2004; Fritsch and Moraru, 2008). Bacteria spores and somatic cells present in raw milk are not affected by the HTST heat treatment used in the processing of most dairy products, whereas they can be physically removed by MF. If not removed or killed, spores can compromise the quality and shelf life of milk and other dairy products, such as milk powder and cheese (Gesan-Guiziou, 2010). At the same time, high SCC can lead to increased proteolytic and lipolytic activity in milk, thus compromising the flavor, texture, and shelf life of dairy foods (Azzara and Dimick, 1985; Verdi and Barbano, 1988; Ma et al., 2000; Te Giffel and Van der Horst, 2004).

The main challenge in milk MF is membrane fouling, which leads to a significant decline in the permeate flux and undesirable changes of membrane selectivity (Guerra et al., 1997). Membrane fouling is caused by the specific physicochemical interactions between the milk components and the membrane. Fouling can occur both because of the deposition of rejected solutes and particles on the membrane surface (external fouling) and to the constriction of pores by feed particles (internal fouling). Particles with diameters much smaller than the membrane pore typically cause pore constriction, those with a diameter comparable to the membrane pore may cause pore blocking, and particles larger than the pores can be retained on the membrane surface and cause cake formation (Fane and Chang, 2009).

Proteins are considered a major contributor to fouling in membrane separation of dairy streams, both due to their interaction with the membrane and due to protein–protein interactions, which lead to formation of agglomerates (James et al., 2003). Brans et al. (2004)

Received January 17, 2014.
Accepted April 7, 2014.
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proposed that in skim milk, MF CN micelles and CN aggregates lead to pore blockage, whereas serum proteins cause adsorption and in-pore fouling. Le Berre and Daufin (1998) concluded that CN are the main factor limiting the flux in MF of milk with a 0.1-μm-pore-size membrane. Nonetheless, several studies reported that serum proteins and their aggregates are almost entirely responsible for membrane fouling in MF of dairy fluids using membranes of sub-micrometric pore sizes (Tong et al., 1988; Kelly and Zydney, 1997; Mourouzidis-Mourouzis and Karabelas, 2006). Regarding the role of individual serum proteins, it was reported that β-LG contributes to fouling because of its tendency for self-association and the formation of dimers and octamers (Kelly and Zydney, 1997; Mourouzidis-Mourouzis and Karabelas, 2006), whereas α-LA has the ability to strongly bind Ca^{2+} (Stuart et al., 1986; Anderson et al., 1997), which results in a calcium-mediated salt bridging between α-LA and the membrane.

Minerals, particularly calcium phosphate, are also considered as one of the leading causes of membrane fouling and flux decline in membrane separation of dairy streams (Hanemaaijer et al., 1989; Gesan et al., 1993). Calcium phosphate precipitate can form deposits on and within the membrane, whereas divalent cations (Ca^{2+}) facilitate protein–protein and protein–membrane interactions (Rice et al., 2009). This is particularly pronounced at high temperatures, which promote precipitation of calcium phosphate. Low temperatures (<10°C) are conducive of micelle disintegration and thus dispersion of calcium out of the CN micelle, also leading to mineral-based fouling.

It has been also suggested that microbial cells can cause fouling by pore blockage in large-pore MF (Brans et al., 2004). Indeed, in the study by Blanpain-Avet et al. (2011) spores and vegetative cell clusters were observed on the membrane surface after the MF of a suspension of *Bacillus cereus* spores with a 0.45-μm ceramic membrane, performed at a cross-flow velocity of 4 m/s. However, Fritsch and Moraru (2008) did not observe any bacteria cells or spores in scanning electron microscope images of a fouled ceramic membrane used in cold MF of skim milk using a 1.4-μm-pore ceramic membrane. This may have been be due to the high cross-flow velocity (7 m/s) used in their study, which possibly prevented the deposition of microorganisms onto the membrane.

Most of the studies mentioned above refer to fouling in small-pore MF (using sub-micrometric pore diameters) of dairy streams. Very little data exist regarding the mechanisms of membrane fouling in large-pore MF of milk, particularly when the process is conducted at low temperatures. As the interest in cold MF of milk is increasing, elucidation of fouling mechanisms could provide insights that would help the development of effective solutions to improve the flux and separation efficiency of this process. The objective of this work was to investigate the mechanism of membrane fouling in large-pore, cold MF of skim milk, focusing on the role of proteins and minerals in external and internal fouling during large-pore MF for microbial removal.

MATERIALS AND METHODS

MF Setup and Experiments

A pilot-scale experimental MF unit that included a feed tank with a capacity of 189 L connected to a variable-speed centrifugal pump, a tubular heat exchanger, a flow meter, and a tubular ceramic membrane placed inside a stainless steel housing was used. The membrane, of Tami design (GEA Filtration, Hudson, WI), had a nominal pore size of 1.4 μm, a length of 1,200 mm, an outside diameter of 25 mm, 23 internal channels with a hydraulic diameter of 3.5 mm each, and a total membrane area of 0.35 m^2. Data acquisition ports were used for collecting the pressure, temperature, and flow rate data. The transmembrane pressure (TMP) was calculated as follows:

$$\mathrm{TMP} = \frac{(P_\mathrm{i} + P_\mathrm{o})}{2} - P_\mathrm{p}, \qquad [1]$$

where P_i is the feed inlet pressure, P_o is the retentate outlet pressure, and P_p is the permeate pressure.

The permeate flux was obtained gravimetrically using an electronic scale connected to the data acquisition system. The permeate flux, J (L/m^2h), was calculated according to the equation

$$J = \frac{M}{A \times t \times \rho}, \qquad [2]$$

where M is the permeate weight (kg), A is the membrane surface area (m^2), t is time (h), and ρ is the permeate density at the operating temperature (kg/m^3).

A total of 117 kg of raw skim milk from the Cornell Dairy Plant (Ithaca, NY) was added to the feed tank. The pump was turned on at low velocity for 20 s to flush out any water that remained in the membrane system after water-flux measurement. After another 70 s, the pump speed was adjusted to a cross-flow velocity (v) of 6.0 m/s, a constant transmembrane pressure of 159 kPa (23 psi) was achieved, and permeate flux data collection was initiated. The MF process was conducted at a temperature of 6 ± 1°C. To maintain temperature control during MF, the milk was passed through a