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On the actual cleanability of polyethersulfone membrane fouled by proteins at critical or limiting flux

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ABSTRACT

The main bottlenecks in ultrafiltration of skim milk are the mastering of fouling and of the following cleaning in place operation nowadays performed during approximately 30% of time at industrial scale. This paper investigates the cleaning efficiency of a polyethersulfone UF membrane of low cut-off fouled at different pressures that allow to cover a large range of flux between the "limiting flux" (favoring a severe fouling mainly due to proteins, an important part of which is highly irreversible) and the critical flux (for the first time evidenced as belonging to the threshold flux type and leading to a lower amount of irreversible proteins matching with the adsorbed quantity without applied pressure). The amount of irreversible proteins, target of the cleaning step, is half when fouling is achieved in threshold conditions than at higher pressures. Then a set of three cleaning in place (CIP) solutions, either chemical or enzymatic, is used with the aim of result generalisation. It is shown that regardless of the chemical intrinsic efficiency of the cleaning solution used, the percentage of removed proteins during the cleaning step depends on the fouling conditions. Finally it can be drawn that the membrane cleanability significantly increases when the fouling is performed in the threshold conditions compared to all other tested conditions.

1. Introduction

Ultrafiltration (UF) is widely used in dairy industry, particularly for the standardization of the protein content issued from skim milk. UF is classically performed with spiral polyethersulfone (PES) membranes of low molecular weight cut-off; typically MWCO is equal to 5–10 kg mol^{-1}. The bottleneck of skim milk UF is the fouling during the production step and the sub-consequent cleaning/disinfecting step. The cleaning step originates at least one third of the environmental negative impacts of the overall process [1]. Consequently, to match with requirements of a sustainable production, a better control of the cleaning step is a real need.

The recent concept of the "critical flux" firstly introduced by Field et al. [2] in 1995 and modified by Field and Pearce [3] in 2011 proposes a theoretical base for the fouling control during filtration. Practical conditions can be found aiming at minimising the irreversible part of fouling. They depend on the judicious choice of the permeate flux (J) during the production step and its correlated transmembrane pressure (TMP).

In a system made of a given membrane and a given fluid to be filtered at a constant cross-flow velocity (v), two particular fluxes, namely the limiting flux ($J_{limiting}$) and the critical flux ($J_{critical}$), are defined. The limiting flux is the maximum flux that can be reached when increasing the TMP [4,5]. The limiting TMP is thus defined as the lower pressure for which this flux can be reached. An increase in TMP above this limiting value does not increase the flux anymore. It is quite well known that in UF of skim milk the fouling at limiting flux is strongly irreversible. Consequently a following cleaning step is needed to restore the membrane performances. Nevertheless, it is nowadays the most common filtration condition applied at industrial scale. Besides this industrial practice, a critical ($TMP_{critical}$, $J_{critical}$) point exists for which the critical TMP and flux are lower than the limiting TMP and flux, respectively. The critical point delimits two fouling behaviours of the membrane [6,7]: below the critical point the fouling is fully reversible whereas above the critical value the fouling turns to irreversibility. Regardless of the filtered fluid, for a permeate flux lower than the critical one, the J versus TMP relationship is always linear. Nevertheless, different experimental curves of J versus TMP are observed, depending on the filtered fluid, and two forms of the critical flux have been initially proposed. They mainly differ by their relative slope at low pressures, when compared to the pure water filtration. For the "strong form", the flux is the same as the water flux and consequently no concentration polarisation phenomenon decreases the flux. For the "weak form", the flux is decreased when compared to the water flux, because of the establishment of a layer due to concentration polarisation.

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As these two initial definitions recently appear to be insufficient, especially when dealing with complex mixtures as food fluids for instance, a complementary case has been recently added; it is called the "threshold flux" [3]. In this last case, at a first glance the J versus TMP curve looks like that of the "weak form", but at a second sight, it can be seen that the flux decrease is not only due to concentration polarisation but also due to little irreversible adsorption of fouling species on the membrane.

The critical flux concept has been shown to be relevant for skim milk filtration, regardless of the filtration type (microfiltration, UF, nanofiltration, reverse osmosis) and extended to filtration of pH modified skim milks (pH range from 3.7 to 11.5) [8–10].

Nowadays, even if the fouling of PES membrane of skim milk UF is not fully understood, we can affirm that it is a multi-layer fouling. Moving from the bulk to the membrane wall, an attempt of description corresponds to (i) a reversible deposit among which is a gel part fully reversible [11,12], then (ii) a cohesive fouling layer strongly adherent to the membrane, made of proteins among which β-lactoglobulin, the main soluble protein of milk, could be the single or at least the main component [11–13]. This strongly attached layer is probably not a mono-layer of proteins adsorbed on the membrane and is the main target of the chemical or enzymatic cleaning. Moreover, depending on the membrane ageing, a soluble protein, namely α-lactalbumin, is able to cross the membrane toward the permeate side and slightly fouled the membrane pores.

According to our knowledge, no systematic study has been achieved to correlate the use of critical conditions during the production step (fouling) and the membrane ability to be cleaned. Only a recent paper [14] has been published dealing with a long term operation of pilot-scale submerged membrane bioreactor for municipal wastewater treatment. As expected, the authors showed that operating at critical flux prevents rapid fouling caused by cake layer formation; moreover the cleaning of the fouled membrane by sodium hypochlorite was shown to be efficient to fully remove the gel layer mainly made of organic compounds.

In this paper the cleanability of an ultrafiltration PES membrane is systematically investigated for different fouling conditions during UF of skim milk.

2. Experimental

A set of three cleaning in place (CIP) solutions, either chemical or enzymatic, is used with the aim of result generalisation. The efficiency of the CIP operation is discussed with respect to the fouling conditions by following the water flux recovery, corresponding to the hydraulic cleanliness evaluation and the residual protein amount determined by FTIR-ATR directly on PES membrane and corresponding to the chemical cleanliness evaluation. The HFK-131 spiral membrane provided by Koch (USA) is selected for the demonstration because it is the main worldwide used membrane at industrial scale for the target application. For sake of simplification experiments are performed in a plate and frame module but membranes of 127 cm^2 filtering area are sampled in a 4333 spiral membrane (the overall area is close to 6.5 m^2) as well as retentate and permeate spacers.

2.1. Solutions

2.1.1. Skim milk and water

The skim milk used is a commercial one (UHT, Lait de Montagne, Carrefour, France) containing an average of 31.5 g L^{-1} proteins and 48 g L^{-1} carbohydrates (mainly lactose) and only tracks of lipids ($<0.5\%$).

Water used either for solution preparation and membrane filtration is deionised and 1 μm filtered. Its conductivity is always lower than 1 μS cm^{-1}.

2.1.2. CIP solutions

Three CIP solutions are used. They are selected because of their different cleaning efficiency toward protein removal.

The first one is a sodium hydroxide solution at pH 11.5 ± 0.1, prepared from NaOH in pellets (analytical grade Normapur, 99%, Prolabo, France). This solution is known to be slightly efficient to remove irreversible proteins on this PES membrane.

Two formulated CIP solutions provided by Ecolab (France) are also used. The concentrations are arbitrary chosen in the range proposed by the provider and the solutions are used as such as obtained without any adjustment of pH. The first one is P3-Ultrasil 10. It is a chemical CIP solution containing at least hydroxide and surfactant(s). P3-Ultrasil 10 is dissolved at 0.4 wt% in water that leads to a natural pH of pH 12.0. This CIP solution was previously shown to be very efficient for this kind of cleaning and is often used at industrial scale. The second CIP solution is an enzymatic mixture, P3-Ultrasil 53. It is prepared at 1 wt%, leading to a natural neutral pH that was not further controlled during the CIP operation. To avoid any enzymatic reaction with components of the food fluid that can be filtered after the membrane cleaning, providers of enzymes recommend finishing the CIP cycle by a nitric acid rinsing step in order to inactivate the enzyme activity. We use either nitric acid or hydrochloric acid at pH 2.5 for this inactivation step.

Nitric acid and hydrochloric acid at pH 2.5 are prepared by dilution of concentrated acids of analytical grade (Normapur, Prolabo, VWR, France).

2.2. Membrane and ultrafiltration loops

2.2.1. Membrane

A PES membrane (5–10 kg mol^{-1}, HFK-131, Koch, USA) in flat (127 cm^2) geometry is used. Flat membranes and spacers (F type, 2 mm) are sampled in a spiral membrane (4333 module).

After removing of preservative by rinsing with warm water, the membrane coupons are conditioned by UF of de-ionized water during 6 h at 46 °C ± 1 °C. During this UF time, TMP is gradually increased from 1 to 4 bar. The obtained plateau value of permeability at 46 °C is used as reference for the pristine membrane.

2.2.2. Plate and frame module and pilot

The plate and frame module (Ray-Flow X100, Novasep-Process, France) allows using two membranes in series. Two new membranes (2 × 127 cm^2) are used for each experiment. Fouling of the two PES membranes is simultaneously achieved by UF of skim milk during 3 h at 46 °C in batch mode (total recycling of both retentate and permeate in the feed tank, corresponding to a volume reduction ratio (VRR) of 1). Thanks to the dead volume of the pilot, the skim milk volume used is chosen to be 4 L. The cross-flow average velocity (v) is close to 0.3 m s^{-1} that is a typical value encountered in a spiral membrane. Moreover polypropylene spacers are added in the liquid vein to provoke local turbulences and favored a high flux as in spiral configuration. Various transmembrane pressures (TMP) ranging from 1 to 4 bar are applied (see results). The membrane flux (J_{UF}) is measured all over the filtration time by weighting a certain volume of permeate in a given time.

After the skim milk UF, the two membranes are carefully rinsed with de-ionized water (no optimization of the used volume) and the final water flux ($J_{irrev,initial}$) is determined for both membranes. After that, only one membrane is demounted