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Cleaning of skim milk PES ultrafiltration membrane: On the real effect of nitric acid step

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ABSTRACT

Cleaning of PES membranes after ultrafiltration of skim milk is still often performed at industrial scale with a formulated alkaline first step followed by a nitric acid step. This cleaning mode gives sufficiently satisfactory results in terms of water flux recovery but cannot prevent a progressive decline of production flux over time. The analysis of the deposit on the membrane by FTIR-ATR highlights the nature of the irreversible fouling, exclusively made of proteins, and the real cleaning efficiency. Sodium hydroxides alone allows up to 24% of protein removal which is in good agreement with the water flux recovery after this treatment. Nevertheless, the amount of protein remains exactly the same after nitric acid treatment whereas the flux significantly grows. This flux increase without any protein removal is strongly dependent on the proteins amount on the membrane at the start of nitric acid step. This phenomenon is not observed with HCl, but it seems not totally specific from HNO_3 as the use of H_3PO_4 in particular leads also to similar results. The specific adsorption of oxoanions on proteins at acid pH that will change the hydrophobicity of the deposit is suspected.

The nitric acid step can be suppressed as it is useless and misleads on the real efficiency of the overall cleaning.

1. Introduction

Ultrafiltration is the process used to standardise the skim milk protein content in dairy industry for the consumption or before cheese making. The high fouling resulting from this application limits the productivity and needs twice daily cleaning operations (2–3 h for 6–8 h of production) to recover an acceptable flux. At industrial scale, cleaning is generally carried out with various empirical sequences performed with more or less complex cleaning solutions including an alkaline (typically sodium hydroxide NaOH with surfactant at pH 11.5) to remove organic matter and a nitric acid step (pH 1.6) to remove the mineral fouling (calcium deposit). An alternative to this chemical, also today more widely used industrially is the enzymatic cleaning [1] that is followed by a deactivation step with nitric acid as recommended by the supplier. This chemical or enzymatic cleaning is followed by disinfection with NaOH and sodium hypochorite (150–200 ppm).

This cleaning mode is justified by quite acceptable results in terms of flux recovery just after the treatment. Nevertheless, it can neither prevent a decrease of the production flux over several months scale nor sometimes an alteration of the membrane selectivity as it is often observed at industrial [2,3].

The cleaning step is clearly identified as a bottleneck of membrane separations due to a lack of knowledge about its fundamental mechanisms that makes its optimisation difficult.

Some works focused on the cleaning of polyethersulfone ultrafiltration membranes used to concentrate whey proteins [4], of polysulfone membrane used to ultrafiltrate pasteurised milk [5,6], reconstituted skim milk [2] whey proteins from whey protein concentrate [7–10], cheese whey [11] and on the cleaning of inorganic membranes [12,13]. But the efficiency of the cleaning sequence is strongly dependent of the couple membrane/ fluid, particularly for complex dairy fluids.

For the ultrafiltration of skim milk, the PES membrane HFK-131 (5–10 kg mol^{-1}) is a worldwide used membrane that represents 70% of the market. A previous study focused on the nature of the fouling on this PES membrane for this application. After skim milk ultrafiltration and rinsing, the analysis of the fouling revealed by SEM–EDX that there are here no minerals. Proteins are then the exclusive target of the cleaning. The nitric acid is

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used after the alkaline cleaning to remove the mineral part (calcium phosphate) of the fouling by industrials that justify its use by the observed flux increase after the treatment with this product.

The question that arises is if there any oxidative action on the residual proteins or any change in the structure of the deposit due to the pH change [4,15].

In this work, a cascade of NaOH followed by HNO_3 is first studied to better understand the action of nitric acid during the cleaning in this given application. The first step with NaOH is certainly not the more efficient to remove the fouling, nevertheless it will highlights the real effect of nitric acid avoiding the impact of formulated alkaline detergent on the membrane hydrophobicity. Indeed surfactants contained in alkaline cleaning products are known to adsorb on the membrane and to increase their flux [16].

The effect of NaOH on the irreversible protein fouling is then first presented and is followed by the study of the second step of the cleaning sequence *i.e.* the nitric acid.

Other solutions are studied to highlights the action of this reagent: sodium nitrate, hydrochloric acid, phosphoric acid, citric acid and sulphuric acid.

The efficiency of both cleaning agents is evaluated in terms of water flux recovery (as in industry) and real protein removal (quantified by FTIR-ATR) in plate and frame and spiral configuration. The effect of nitric acid is finally presented in a biological cleaning where it used to inactivate the enzyme at the end of the cleaning process.

2. Experimental

2.1. Fluids

The UHT skim milk (Lait de Montagne, Carrefour, France) chosen contain an average of 31.5 g L^{-1} of proteins and 48 g L^{-1} of carbohydrates as well as minerals, close to 8 g L^{-1}.

In this study several single solutions were used: sodium nitrate at 8.5 g L^{-1} and pH 6.6, nitric acid at pH 1.6 (65% analytical grade, Acros), hydrochloric acid at pH 1.6 (37% analytical grade, Acros), phosphoric acid at pH 1.6 (85%, Fisher), citric acid at pH 1.8 (Fisher), sulphuric acid at pH 1.6 (95–97%, Fluka), sodium hydroxide at pH 11.5 (pellets 97% Rectapur, Prolabo) and a chlorinated alkaline one with 200 mg L^{-1} of active Cl_2 prepared from a stock NaOCl solution (bleach 37° Cl_2, Lacroix) adjusted with NaOH at pH 11.5.

The enzymatic cleaning was lead with P3-Ultrasil 53 (Ecolab). It was prepared at 1 wt% leading to a natural neutral pH. As the latter parameter was not regulated during the cleaning, the operating conditions were probably not perfectly the optimal. As recommended by providers, a nitric acid rinsing was done after the treatment to inactivate the enzyme activity. Nitric acid at pH 2.5 is usually suggested but HCl was also tested at the same pH.

Water used for preparation of cleaning solutions was filtered (1 μm) and deionised.

2.2. Membrane

The spiral UF membrane used was made of polyethersulfone (PES, HFK-131, Koch, 6.5 m^2) with a MWCO of 5–10 kg mol^{-1}. The spiral membrane was stored in sodium metabisulphite solution (5 g L^{-1}, Acros, analytical grade) after each experiment to avoid any microorganism growth.

Flat membranes (0.0127 m^2) were also used as model for spiral membrane in order to quantify protein fouling by FTIR-ATR. Before use, flat membranes were first rinsed 10 min in methanol to remove the conservative (glycerol) and were then rinsed with deionised water. A new pristine membrane was used for every new UF and was compressed by fluxing water for 1 h at a transmembrane pressure of 4 bar before the water reference flux was measured.

2.3. Ultrafiltration process

2.3.1. Spiral-wound pilot

A pilot of 100 L capacity (TIA, Bollène, France) equipped with the spiral membrane HFK-131 [standard size 25–40, 6.5 m^2, spacer of F type (2 mm)] was used. The fouling of the membrane was performed at 2 bar with a recirculation rate fixed at 10.5 m^3 h^{-1} corresponding to a cross-flow velocity of about 0.3 m s^{-1} (as at industrial scale).

24 L of skim milk were ultrafiltered during 150 min at transmembrane pressure $TMP=2$ bar and 50 °C with a volume reduction ratio $VRR=1$ (batch mode).

Water rinsing was preceded by a total draining of the pilot and achieved at the minimal pressure allowed by this pilot (0.2 bar) at 150 L h^{-1} (i.e. a cross-flow velocity about 0.008 m s^{-1}). In the first step, the module was rinsed with 70 L of filtered tap water (active carbon and 1 μ filter) that was discarded towards waste. Then, in the second step 50 L of deionised water were recirculated in the loop during 20 min with the permeate discarded.

Cleaning of the membrane by 25 L (3.8 L m^{-2}), if not specified, of cleaning solution was performed 60 min at 50 °C in the same hydrodynamic conditions as the fouling.

A second rinsing, as described before, was realised before a water flux measurement.

2.3.2. Plate-and-frame module

The tangential plate and frame UF module (Ray-Flow X100, Orelis) presented an effective membrane surface of 0.0127 m^2. Flat membranes as spacers (F type, 2 mm) were recovered from a commercial spiral module. The fouling was achieved by UF at $VRR=1$ of 4 L of skim milk during 150 min at 50 °C and 2 bar. The following water rinsing was performed in 2 steps after draining the pilot, in order to minimise the water consumption. First, during 2 min rinsing was performed without recirculation of permeate and retentate and then, during 30 min, only retentate was recycled. The following cleaning was made with 4 L of solution. The pilot and the membrane were then rinsed with water until a neutral pH was reached both in the retentate and the permeate.

A second rinsing was proceed before the measure of the after-cleaning water flux.

The 3 steps of a set of experiments were always performed in the same hydrodynamics conditions: cross-flow velocity $v=0.3$ m s^{-1} at 2 bar and 50 °C for fouling, water rinsing and cleaning.

2.4. Evaluation of cleaning efficiency

At least two replicates of each cleaning experiments were done in spiral and in plate and frame configuration. Each time, water flux recovery and residual protein amount were evaluated.

2.4.1. Water flux recovery

The water flux recovery was the ratio of the water flux after the chemical treatment and a rinsing (J) on the reference water flux (J_0) that corresponded to the pristine membrane well cleaned and rinsed. The accuracy on flux measurement was better than 3% (coefficient of variation).

$$\text{Water flux recovery} = J/J_0$$

The hydraulic cleanliness is reached when the water flux recovery is up to 90%. The relative error on this parameter was 5%.