RECOVERY OF PROTEINS FROM DAIRY EFFLUENTS BY MEANS OF ULTRAFILTRATION

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ABSTRACT

The purpose of this work was to investigate the potential of membrane ultrafiltration for the recovery of proteins from dairy effluents. Employing a 10 kDa tubular ceramic membrane in total recycle and batch modes, the effects of temperature, feed flow rate, and protein concentration in feed were evaluated by measuring permeate flux-transmembrane pressure and permeate flux-time profiles, and total protein rejection coefficients. Results from these experiments have been used to analyze the technical viability of the recovery of dairy proteins by ultrafiltration. Last stage of the work consisted of a preliminary analysis of different phenomena limiting flux in this system. For this reason, previous experimental data were fitted with mathematical models proposed in bibliography by means of a computer tool of our own programming. Furthermore, a thermo-chemical washing method was successfully applied to clean tubular ceramic membranes previously fouled with dairy solutes.

Keywords: Milk proteins; Ceramic membrane; Ultrafiltration.

1. INTRODUCTION

Present study places inside a very recent research line of the Department of Chemical Engineering in the Faculty of Environmental Sciences of University of Castilla-La Mancha (Spain) about reclamation of dairy effluents by means of ceramic tubular membranes.

Milk can be considered as an emulsion of fat globules in an aqueous phase. The aqueous phase consists of suspended and dissolved components, such as casein micelles, serum proteins, lactose and salts. Besides the major components (fat, casein and lactose), milk contains valuable minor components that can be interesting for their specific isolation (Brans et al 2004). Molecular weights and sizes of the components of a typical whole milk are shown in Table 1.

The dairy industry was pioneer in the development of ultrafiltration (UF) equipments and techniques to fractionate the proteins from whey and to make cheese from ultrafiltered milk. Application of UF in the dairy industry started with the separation and concentration of whey proteins from whey in 1972 (Atra et al 2005).

Table 1. Molecular sizes of milk components (Cheryan and Alvarez 1995).

Component	Molecular weight (Da)	Diameter (nm)
Water	18	0.3
Chloride ion	35	0.4
Calcium ion	40	0.4
Lactose	342	0.8
α-lactalbumin	14,500	3
β-lactoglobulin	18,000	4
Bovine Serum Albumin	69,000	5
Casein micelles (milk protein in solution)	107,000-109,000	25-130
Fat	-	2,000-10,000

Whey is the liquid remaining after the recovery of cheese. Whey contains more than the half of the solids of the original whole milk, including whey protein (20 % of total protein) and most of the lactose, minerals and water-soluble vitamins. The principal aim of UF of whey is to concentrate the native or pre-denatured whey proteins in order to obtain a whey protein powder with varying protein content and reduced lactose and ash contents (Da Costa et al 1993, Huffman 1996).

In UF the constituents of milk are fractionated according to molecular size. Depending on the retention characteristics of the membranes there can be a significant difference in the nutritive power of the retentate and permeate. The protein and fat fractions are retained very well (virtually completely) in the retentate, while the lactose, minerals and vitamins are divided between the retentate and the permeate (Hinrichs 2001).

UF has been as well used to recover valuable components from dairy waste streams (Khider et al 2004, Rektor and Vatai 2004). For example, dairy proteins are valuable products and are used as high-value food additives, nutraceuticals and therapeutics (Chollangi and Hossain 2007).

Unfortunately, current membrane processes for milk have a rather low capacity due to the strong flux decline by fouling. These processes are usually energy demanding because of the high cross-flow velocity that is required to control fouling (Brans et al 2004).

Fouling of UF membranes in the dairy industry is mostly due to precipitation of micro organisms, proteins, fats and minerals on the membrane surface. Formation of a cake or gel on the membrane surface or into the membrane pores increases fouling due to the fact that present pores are (partially) blocked or become narrow, and finally this reduces the permeate flux (Kazeminoghadam and Mohammadi, 2007). Calcium phosphate is the predominant foulant at various fouling conditions, with other components including whey protein and lactose playing a lesser role. This is evidenced by the trends in bulk and soluble calcium concentration during filtration. pH value has been also shown to have a

greater influence on flux decline than temperature, with high fouling observed for conditions of high pH values (Rice et al 2006).

Due to fouling, cleaning of the membranes is essential (Chollangi and Hossain 2007). Cleaning can be usually performed in 3 forms: physical, chemical and biological (Trägardh 1989). Chemical methods are used most often. Chemical cleaning agents must be able to dissolve most of the precipitated materials and take them away while they should not damage the membrane surface (Lindau and Jönsson 1994). Some of these cleaning agents are acids, alkalis, surfactants, disinfectants and combined cleaning materials (Trägardh 1989). While using these materials as cleaners, the effect of some parameters such as pH, concentration and washing time (Lindau and Jönsson 1994) and operating conditions like cross-flow velocity, transmembrane pressure and temperature (Bohner and Bardley 1992, Daufin et al 1991) must be considered. In order to clean the membranes fouled with milk and whey, one alkali washing step followed by an acid washing step has been suggested (Daufin et al 1991), and to get better results one enzyme washing step could be used before chemical washing.

The aim of this research work was to study the effects of temperature, feed flow rate and protein concentration in feed on the recovery of milk proteins from synthetic diluted effluents from dairy industry. Different phenomena limiting permeate flux were analysed, and a method of chemical cleaning was tried. The use of tubular ceramic membranes is another novelty with regard to existing research, since a majority of studies of this kind at lab scale were developed with polymeric flat membranes (Atra et al 2005, Chollangi and Hossain 2007, Kazeminoghadam and Mohammadi 2007, Rabiller-Baudry et al 2007, Rice et al 2006), while operation at industrial scale is usually performed with ceramic membranes, because of better resistance of these membranes against cleaning and disinfection (Brans et al 2004).

2. MATERIALS AND METHODS

2.1. Fluids and cleaning procedure

Synthetic milk effluents were prepared with a solution of commercial whole cow milk powder (UHT, Central Lechera Asturiana, Spain). Total protein quantification in permeate and retentate streams was performed using the well-known *Biuret's method* (Gornall et al 1949).

After each experiment with milk solution, the membrane was thermo-chemically cleaned with an alkaline solution (NaOH 0.125 M; T = 75 °C; cross-flow velocity, v = 2 m/s; transmembrane pressure, TMP = 2 bar; 60 min) in first place, and then with an acid one (HNO_3 0.1 M, T = 50 °C, v = 2 m/s, TMP = 2 bar, 45 min), until the clean membrane resistance was recovered. Rinsing stages with distilled water (T=25 °C, v=3 m/s, TMP=0 bar, 20 min) were inserted before and after alkaline cleaning, and after acid cleaning.

2.2. Set-up

A laboratory-scale installation was used for UF experiments. This installation consisted of a 2 litres jacketed glass tank (1), a Liquiflo 37 F gear pump (2), a Selecta Frigiterm-10 circulation ultrathermostat (3), a Techfluid flowmeter (60-630 l/h) (4), a Novasep Micro Carbosep 40 module with a Carbosep M5 tubular membrane (zirconia, MWCO 10,000 Da,

$8 \cdot 10^{-3}$ m^2, internal diameter $6 \cdot 10^{-4}$ m, 0.4 m length) (5), two Bourdon manometers (6) and a needle valve (7). A diagram of this installation is pictured in Figure 1.

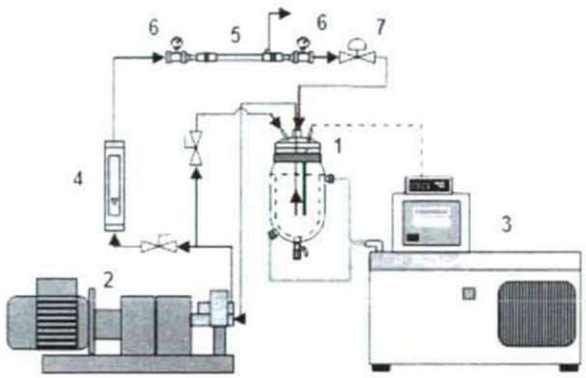

Fig.1. Diagram of installation of UF.

3. RESULTS AND DISCUSSION

3.1. Total recycle experiments

For the first time, influence of temperature, protein concentration in feed and feed flow rate on permeate flux and total protein rejection coefficients were analyzed by total recycle (constant composition) experiments, in which retentate and permeate were continuously returned to the feed tank.

Some results from these experiments are depicted in Figures 2 and 3. As can be deduced from these plots, three different measures can be performed in order to improve permeate flux: an increase in temperature, a decrease in protein concentration in feed and/or an increase in feed flow rate.

The effect of temperature on the permeate flux can be understood from its effect on the properties of the feed stream. Increasing the temperature results in a decrease in the viscosity of milk, resulting in an increase in permeate flow rate according to Hagen-Poiseuille law (Chollangi and Hossain 2007, Rice et al 2006). Nevertheless, operating temperature should not be higher than 50 °C, because it can cause heat denaturation of the whey proteins (Atra et al 2005).

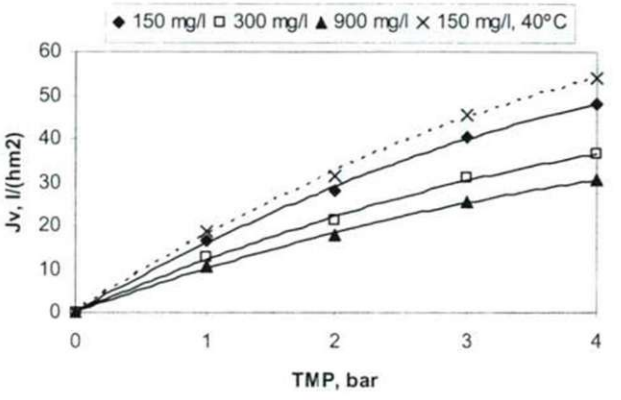

Fig. 2. Permeate flux profiles at v=1 m/s, at different protein concentrations in feed stream (— 25°C, ---- 40 °C).

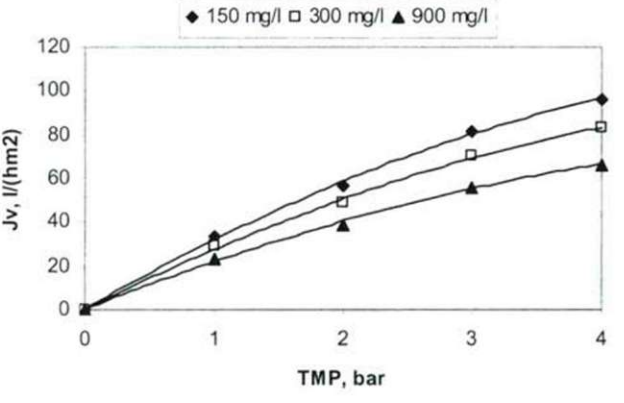

Fig. 3. Permeate flux profiles at v=3 m/s, temperature 25 °C at different protein concentrations in feed stream.

For all protein concentrations essayed, it is observed that the permeate flux increased up linearly to a transmembrane pressure of 2-3 bar, after that it reached a plateau when the TMP increased from 3 to 4 bar. This could be attributed to the gradual build-up of protein and similar molecules on the membrane surface nullifying the effect of an increase in pressure (Chollangi and Hossain 2007). The higher concentration of protein in the milk systems seems to promote concentration polarization which controls permeate flux (Ramachandra Rao 2002). Above a critical TMP (3-4 bar) the flux becomes almost independent of pressure, because the protein molecules deposited on the surface of the membrane cause a concentration polarization controlled by two factors, the type of membrane and the cross-flow velocity (Atra et al 2005).

In this way, in Figures 2 and 3 we can see that as cross-flow velocity increases, concentration polarization decreases, hence the point of pressure independence advances to

higher pressures (TMP 2 bar at v=1 m/s, TMP 3 bar at v=3 m/s). This phenomenon is in agreement with literature data (Kessler 2002). Higher flow rate at the membrane surface is a very important factor in increasing permeate flux. Using higher velocity the deposited molecules are continuously removed from the membrane surface and thus the hydraulic resistance of the fouling layer is reduced.

There are different methods which can be used to generate high turbulence: increasing the feed flow rate, decreasing the flow channel dimensions or insertion of a static mixer (Atra et al 2005). It is obvious that the flux increases at higher cross-flow velocities because there is a decrease in the deposit layer resistance. Continued gain in flux is limited by energy, which can be afforded in pumping, but we must take into consideration that there is the danger of damaging the fat globules by excessive pumping.

The trends observed in Figures 2 and 3 can be also related to the concept of "critical" flux. It is the upper flux to obtain reversible deposit of foulant on a membrane, and it was proposed in the early 1990s' (Field et al 1995). A more practical concept of "sustainable" flux was more recently defined as the upper flux to obtain reversible deposit on a constant fouling layer (Bacchin et al 2005, Manttari et al 1997).

According to the "critical" flux theory (Field et al 1995, Howell 1995), three regimes can be distinguished for membrane filtration, according to transmembrane pressure dependence of flux. In regime I, the transmembrane pressure is below the critical pressure and there is cake free filtration. Two forms of critical flux exist: the hard form, where the flux/pressure relation is linear and equal to the clean water flux; and the weak form, where the flux/pressure relationship is still linear, but lower than for clean water flux. Filtration in this regime is advised to obtain optimal selectivity. However, because of the low value of the flux, the capacity is low and a large membrane area is needed. According to Figures 2 and 3, this is the regime of operation for the totality of experiments under TMP 2 bar for v=1 m/s and under TMP 3 bar for v=3 m/s.

In regime II, the transmembrane pressure is above the critical pressure and flux is equal to the limiting flux, which can be described by the gel filtration model or back-transport models (Belfort et al 1994), as the transport of materials towards the membrane is in equilibrium with the back transport towards the cross-flow. Hence, a higher cross-flow velocity is advantageous and could even shift the process to regime I. Furthermore, the flux is independent of the transmembrane pressure and the pore size of the membrane (Brans et al 2004). It is the case of experiments carried out at TMP higher than 2 bar for v=1 m/s, and 3 bar for v=3 m/s.

In regime III, transmembrane pressure is clearly above the critical pressure and results in a time dependent flux, mostly attributed to cake compaction. For long time stable operation in regime III, it is necessary to remove fouling after short intervals.

Concentration of whey protein usually takes place in regime II, to have optimum capacity, whereas the isolation of whey proteins is restricted to regime I, for optimal selectivity (Brans et al 2004).

Regarding total protein rejection coefficients, values within the range 0.92-0.99 were obtained in all experiments (Atra et al 2005, Chollangi and Hossain 2007), except for experiment at 40°C, where rejection coefficient decreases dramatically until 0.49.

The reason is high temperature increases the solute diffusivity and the rate of transport of solutes from the membrane surface into the permeate stream (Chollangi and Hossain 2007, Rice et al 2006). According to MWCO of membrane used and typical composition of milk (Table 1), retentate stream will be constituted by α-lactalbumin, β-lactoglobulin, BSA, casein and fat (Brans et al 2004, Chollangi and Hossain 2007).

3.2. Batch experiments. Factors limiting permeate flux.

Once viability of proposed method for the retention of milk proteins has been proved in total recycle experiments, we made use of batch experiments in order to increase protein concentration in solution to treat and to study factors limiting permeate flux. For this, influences of initial protein concentration, feed flow rate and temperature on permeate flux-time profiles (Figs. 4 and 5) and protein concentration in feed-time profiles (Figs. 6 and 7) were analyzed.

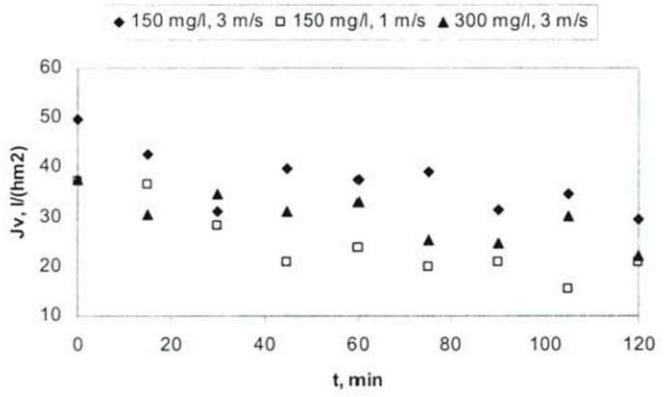

Fig. 4. Permeate flux-time profiles at temperature 25 °C, different initial protein concentrations and cross-flow velocities.

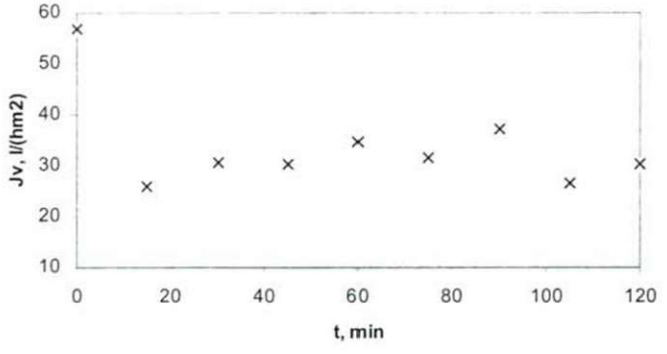

Fig. 5. Permeate flux-time profile at temperature 40 °C, initial protein concentration 150 mg/l and cross-flow velocity 3 m/s.

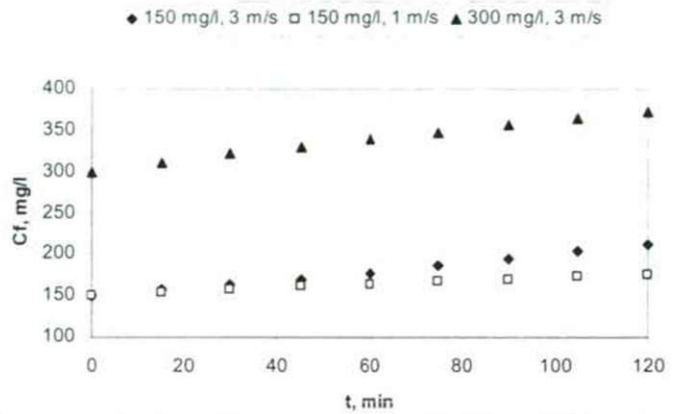

Fig. 6. Protein concentration-time profiles at temperature 25 °C, different initial protein concentrations and cross-flow velocities.

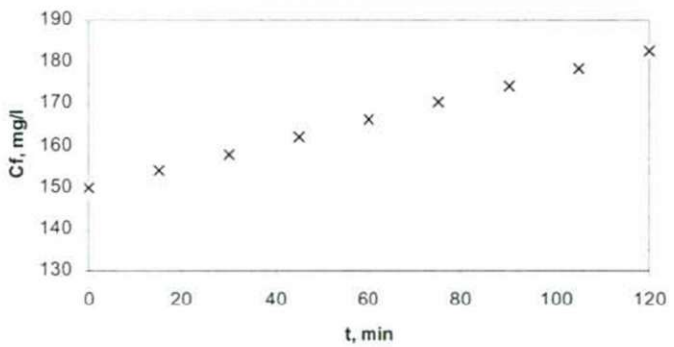

Fig. 7. Protein concentration-time profile at temperature 40 °C, initial protein concentration 150 mg/l and cross-flow velocity 3 m/s.

Generally speaking, we can observe that protein concentration is better developed in experiments with initial concentration 150-300 mg/l, v=3 m/s and 25 °C. In experiment with higher temperature (Fig. 5), initial flux is maximum but fouling appears before, and for experiment at v=1 m/s, permeate fluxes are minimum for all operation time.

In all cases the permeate flux decreases with time. This is expected as the components from the wastewater sample become more concentrated and they can be adsorbed on to the membrane surface and causes such decrease. The permeate flux seems to level off at around 30 l/h·m^2 after 60 min when v=3 m/s, and 20 l/h·m^2 when v=1 m/s. Steady state has been achieved after initial fouling because the rate of adsorption of molecules on the membrane surface is equal to the rate of molecules removal from the surface due to the cross-flow (Chollangi and Hossain 2007).

As it was aforementioned, one of the major factors influencing the economical feasibility of membrane separation technologies is the rate at which fouling occurs. Permeate flux declines due to the contribution of the various fouling processes (James et al 2003).

Different fouling mechanisms can take place: adsorption, pore blocking, cake layer formation, and depth fouling (Brans et al 2004). Concentration polarization is strictly speaking not fouling, but also decreases the flux and can affect selectivity, since rejected particles can accumulate at the surface of the membrane due to their slow diffusion back into the retentate, causing a concentration gradient at the membrane surface. The concentration at the surface can exceed that required for gel formation resulting in a gel layer. This layer alters the resistance of the membrane and, possibly, the sieving characteristics also.

Short-time reversible fouling takes place on a small time scale (seconds, Guerra et al 1997) and can be avoided by the right choice of process conditions, such as high cross-flow velocity or back-pulsing. Pore blocking and cake formation are typically considered short-time reversible fouling. Long-time reversible fouling causes a slow flux decrease in time (hours) and can be removed by stopping the production process and applying a cleaning procedure. Irreversible fouling causes flux decline and cannot be removed by cleaning (Brans et al 2004).

According to bibliography, when in feed there are low levels of proteins (as in the beginning of our batch experiments), flux is controlled by the fouling resulting from gradual adsorption of dairy proteins to the membrane surface and pore plugging by precipitated calcium phosphate (Ramachandra Rao 2002).

In some previous studies, it was checked that the pore blocking model as well as the cake model were not able to describe the fouling of membranes in UF of dairy effluents (Rabiller-Baudry et al 2007). Nevertheless, because of the relative size of membrane pores and proteins, it is obvious that fouling due to proteins mainly occurs on membrane surface and not into the pores. It is reported that apolar interactions involving proteins are responsible of the cohesion of the fouling layer (Rabiller-Baudry et al 2007).

With feeds with higher levels of proteins (as in the end of our batch experiments), the formation of a concentration polarization layer brought the initial flux to lower levels, but they reach a plateau without change during 1 h of UF run (Ramachandra Rao 2002).

For this reason, final experimental data of batch runs have been fitted according to thin film concentration polarization theory, where k is mass transfer coefficient (m/s), C_m is concentration at membrane, C_f and C_p are concentrations in feed and permeate, respectively (Cañizares et al 2002).

$$J_v = k \ln\left(\frac{C_m - C_p}{C_f - C_p}\right) \qquad (1)$$

With this equation, we have obtained values of k in the range of $1.0 \cdot 10^{-5}$ m/s (for experiment with 150 mg/l and v=3 m/s) and $2.5 \cdot 10^{-6}$ m/s (150 mg/l, v=1 m/s). In the case of experiment at 40 °C, mass transfer coefficient is similar to the corresponding experiment at 25°C, but C_m is almost twice bigger.

3.3. Cleaning process

During the ultrafiltration of dairy solutions a more or less important overall fouling happens, leading to a strong decline of permeate flux. After water rinsing, some materials which are not chemically adsorbed on the membrane surface can be washed with distilled water (Madaeni et al 2001), but long-time reversible and strong irreversible fouling remained generally on membranes. A chemical cleaning is needed in order to restore partially the flux (Rabiller-Baudri et al 2007).

According to bibliography, acids are the weakest cleaning agents for fouling with dairy effluents. Results show that alkaline solutions have a moderate effect, but combinations of chelating agent, surfactant and alkali provide the best cleaning efficiency (Kazeminoghadam and Mohammadi 2007).

In this study, we have made use of a combination of an alkali agent (sodium hydroxide 0.125 M; T = 75 °C; cross-flow velocity, v = 2 m/s; transmembrane pressure, TMP = 2 bar; 60 min) and an acid agent (nitric acid 0.1 M, T = 50 °C, v = 2 m/s, TMP = 2 bar, 45 min). Alkaline cleaning is known to be efficient toward organic matter whereas acid solution is known to be efficient toward mineral matter (Rabiller-Baudri et al 2007). Autopsy of different membranes at the end of service life in UF of dairy products (Rabiller-Baudri et al 2002) showed that proteins were the main components of the irreversible fouling and consequently the main target of the cleaning.

It seems that the cleaning agent diffuses into the deposited cake layer on the membrane surface. Diffusion rate depends on different factors including turbulence. A chemical reaction occurs between the cleaning agent and the deposited materials at the membrane surface. The reaction may be hydrolysis, dissolution or dispersion. This results in removal of fouling materials from the membrane surface (Kazeminoghadam and Mohammadi 2007).

Other reported results evidenced that water rinsing must be taken into account in the whole efficiency of the cleaning (Rabiller-Baudry et al 2007). For this reason, before both alkaline and acid cleanings, and after acid cleaning, membrane was rinsed with distilled water for 20 min (T = 25 °C, v = 3 m/s, TMP = 0 bar).

In all cases it was observed that clean membrane resistance was successfully recovered after cleaning process. Obviously, this process was only applied when pure water flux of fouled membrane was lower than the advisable value provided by membrane manufacturer (170 l/h·m^2 at TMP 4 bar and 25°C).

4. CONCLUSIONS

We can conclude that proposed UF method is viable for the recovery of proteins from diluted synthetic dairy solutions. Furthermore, according to our results, feed flow rate is the key parameter to fight against membrane fouling and concentration polarization.

Nevertheless, in order to develop future research, it would be important to analyze the influence of pH value on permeate fluxes and protein rejection coefficients.

Rice et al (2006) report that an increase in pH value and temperature decreased permeate flux, since calcium phosphate will precipitate from solution, and this precipitate will likely to settle onto the membrane in the form of a mineral cake layer.

Furthermore, adjustment of pH and addition of salt influence the electrostatic and steric interactions between different proteins, and between proteins and the membrane (Cheang and Zydney 2003).

As summary, pH value could be a good method to control membrane fouling during ultrafiltration of dairy effluents (Ramachandra Rao 2002).

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