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Fluxes in reverse osmosis of model acidic and alkaline transient effluents issued from skim milk filtration

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ABSTRACT

The flux behaviour in reverse osmosis of natural and modified skim milks corresponding to more or less concentrated transient effluents with pH varying in the range 3.5–11.5 was in-depth studied. For critical and limiting filtration conditions, the origin of flux decline, namely concentration polarisation, gel formation, irreversible fouling and osmotic pressure effects, was discussed with respect to the pH variation inducing physico-chemical variations in the complex equilibrium existing in these fluids. At lower fluxes, corresponding to sub-critical conditions the flux decrease was shown to be mainly due to osmotic effects. At higher fluxes corresponding to limiting conditions, the flux decrease was equally shared by osmotic pressure and other reversible phenomena (concentration polarisation and gel) and irreversible fouling. Fouling resistances appeared to be correlated to casein micelles deposit as the increase of casein net charge could be in good agreement with the increase of the porosity of the fouling deposit. Moreover, the fouling resistance increased with the calcium and phosphate soluble fractions in modified skim milks and mainly with free calcium appearing as the main promoter of the mineral fouling in/on the membrane.

Keywords: Reverse osmosis; Limiting flux; Critical flux; Caseins; Milk; Effluents

1. Introduction

Except for the chemical industry, the food industry, and in particular dairy, is the main sector responsible for industrial pollution. There are two categories of dairy effluents, namely "source separated" or overall ones. Effluents separated at source correspond to dairy matter diluted by water during rinsing steps, without significant variation of the pH of natural milk (6.6–6.7). Overall effluents include water diluted dairy matter and solutions issued from the several cleaning steps. The pH of effluents can vary in a wide range between 1.6 and 11.5 according to the cleaning step (acidic or alkaline one). Reverse osmosis (RO) is able to treat the "source separated effluents" in order to prepare water that can be reused directly in the dairy plant for applications without food contact [1–3]. After an appropriate treatment by the membrane, the overall effluents could be recycled for cleaning purpose [4–5].

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To check the criteria of a sustainable process, RO of the dairy effluents must lead to both high fluxes and high retention of chemical oxygen demand (COD). Moreover, the RO spiral membrane must be easy to clean. The best way to achieve such objectives is to control the whole fouling that limits the flux, and the irreversible part of the fouling that governs the cleaning time.

It is quite well known that casein micelles, the colloidal part of proteins in milk, are the major component of membrane fouling when dealing with skim milk filtration. Thus dealing with flux mastering corresponds more or less to deal with the complex structure of these proteins and consequently that of the induced fouling layer. Individual caseins are small proteins ($20{,}000\,\mathrm{g\,mol^{-1}}$). In milk, they are associated in a quite complex structure called "caseins' micelle" or "caseins' micelles" or "native caseins' micelles". At natural pH of milk, the average size of caseins' micelle is close to 210 nm [6,7]. The colloidal structure of the micelles is stabilised by phosphocalcic bridges between phosphoserine groups of individual caseins and very small inorganic regions made of calcium phosphate. Such inorganic parts of the micelles' structure have recently been called nanoclusters. Soluble globular proteins (close to $5\,\mathrm{g\,L^{-1}}$) are also dissolved in the aqueous part of milk. Moreover, mixture of various salts (close to $8\,\mathrm{g\,L^{-1}}$) is also dissolved in this aqueous phase. Among them are phosphate, citrate, chloride, potassium, sodium, magnesium and calcium. Very complex balances exist between the various constituents of milk. Small variation of the pH and/or of the concentration (water dilution) can lead to versatile forms of caseins and associated salts that could be further promoters of fouling. On one hand, when decreasing the pH, the native micelles tend to disappear, leading to aggregates of different sizes at their isoelectric pH (pH = 4.6). On the other hand, when increasing the pH, the native micelles are progressively disrupted leading to aggregates of various sizes; at least individual caseins can be obtained that is accompanied by the disappearance of the white colour of milk. Variations of the pH modify not only the size but also the net charge of caseins. Regardless of their forms (individual, native micelles, soluble aggregates), variations of the electrophoretic mobility are evidenced (the electrophoretic mobility is proportional to the charge to size ratio and is experimentally measured).

In the past, RO of skim milk was extensively studied to understand the skim milk concentration process [6,7]. The quick formation of a fouling layer exhibiting properties similar to those of a membrane-like film forming a barrier against the permeation of water and dissolved substances was proposed. This layer is mainly made of proteins but calcium and phosphate play a role on the kinetic of deposit formation and on the cohesion of the whole fouling layer, considered as a non-porous one [8,9]. Moreover, addition as well as removal of calcium lead to an increasing resistance of the fouling lowering the permeate flux [10].

According to our knowledge, only few studies have investigated the filtration behaviour of modified skim milk in the wide pH range from pH 3.5 to pH 11.5. This pH range is considered in this study in order to model overall effluents (alkaline pH) as well as transient ones (both acid and alkaline pHs). These studies have been performed by our own team in ultrafiltration (UF), nanofiltration (NF) and RO, but the in-depth studies are mainly focused on UF [6,7].

Cross-flow filtration at critical flux is a new concept that was proposed in 1990s for a sustainable production instead of filtration at limiting flux [11,12]. The critical flux (J_{critical}) is the maximum flux below which only a reversible deposit fouled the membrane during filtration, while the limiting flux (J_{limiting}) is the maximum flux available during filtration and for which a strongly irreversible deposit is formed on the membrane. Such an irreversible deposit is generally hard to control and to remove during further cleaning steps. Modern trends upon filtration management use this concept leading to recommend filtration in subcritical conditions instead of limiting ones as currently performed at industrial scale. Nevertheless, real mixtures are quite complex, often far from model solutions used for initial proposal of this concept and thus needing more or less important adaptation to be transposed at industrial scale. Membrane processes using natural and modified skim milks are particularly attractive for an in-depth study on real mixtures.

Extended studies have been performed in the past to study the filtration stability both in microfiltration (MF) and UF of dairy products [6,13–15]. Regardless of the considered fluid, studies dealing with critical conditions of filtration are generally achieved by varying hydrodynamic parameters such as transmembrane pressure (TMP), cross-flow velocity (v), shear rate and shear stress. Only few studies deal with the impact of the physico-chemical environment in complex media, and particularly in dairy fluids [6,13,14].

Electrostatic repulsions, involving caseins, have been shown to rule the fluxes variations in the 3.2–11.5 pH range. For extreme pHs, namely lower than 5.0 and greater than 6.7, the caseins' size changes quite strongly and their electrophoretic mobility varies between zero and about ($-1.9\times10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$) [6,7,16], respectively. In such conditions, both limiting and critical fluxes variations with the pH depend on size variations and no more on charges.

Except the highlighting of caseins characteristics on flux variations, no detailed explanations were given in the case of RO of modified skim milks.

The main difference with UF would be the membrane structure as UF organic membranes are porous, whereas RO membranes are dense. Consequently, the in-depth explanation of the fouling location could be different: in UF, it could occur inside/outside the membrane, whereas proteins are not able to enter the RO membrane structure.

Finally, as the behaviour of caseins' micelles and caseins' micelles in concentrate layer is still not completely understood [17,18], it is the same for their consecutive impacts on filtration processes. Thus complementary in-depth studies are always needed to be able to better master the filtration and to prove if there is a real interest in the implementation of limiting flux to the critical flux on an industrial scale.

This paper deals in a more detailed way with analyses of limiting and critical fluxes in the case of RO of modified skim milks in the pH range 3.5–11.5. Classical approaches based on concentration polarisation, osmotic pressure and irreversible fouling, not previously taken into consideration, are shown as well as a discussion concerning various forms of calcium and phosphate that are the main inorganic components entering the composition of the fouling layer in these media together with proteins.

2. Materials and methods

2.1. Fluids

HCl (Acros, for analysis) as well as NaOH (pellets, Prolabo, rectapur 97%) are used for stock solutions ($1\,\mathrm{mol\,L^{-1}}$ or $2\,\mathrm{mol\,L^{-1}}$).

Water for solutions and membrane rinsing is twice filtered (5 µm on active carbon filter then on a 1 µm filter) and deionised.

The natural skim milk used is commercially available (UHT, Lait de Montagne, Carrefour, France). It contains an average of $31.5\,\mathrm{g\,L^{-1}}$ proteins (among them $27\,\mathrm{g\,L^{-1}}$ caseins) and $48\,\mathrm{g\,L^{-1}}$ carbohydrates (mainly lactose, $342\,\mathrm{g\,mol^{-1}}$). The content of various salts (at ca. $8\,\mathrm{gL^{-1}}$) is in good agreement with common literature data [19]. As expected, the natural pH of skim milk is close to pH = 6.6–6.7.

Modified skim milks (model effluents) are prepared by adjusting the pH by slow addition of stock solutions of HCl or NaOH under gentle magnetic stirring, in order to reach physico-chemical equilibrium involved in milk and avoid local irreversible phenomenon. About 1.5 h are needed to obtain 10 L of solution, that must be prepared just before RO to avoid any micro-organism growth at some favourable pHs. Such a preparation also prevents protein hydrolysis at higher alkaline pHs.

Sometimes the natural skim milk is diluted without pH modification. These solutions correspond to particular compositions of modified skim milk thanks to the modification of physico-chemical balances already mentioned in the Introduction.

Finally, some modified skim milks are obtained by both dilution and pH adjustment up to 11.5.

When not said in the text, modified skim milk only refers to pH modifications without any additional dilution.

2.2. RO: set-up, filtration conditions and retention evaluation

The spiral RO membrane ($2.5\,\mathrm{m^2}$) is a TFC HR (NaCl retention of 99.5%) from Koch (USA). The RO experiments are performed with a pilot (TIA, Bollène, France) equipped with a feed tank of 50 L capacity. The membrane fouling step consists in the RO of 10 L of natural or modified skim milk at different TMPs (TMP from 7.5 to 30 bar), with a volume reduction ratio (VRR) = 1 (both retentate and permeate are fully recycled in the feed tank) and a temperature of 25°C. The feed rate is $0.8\,\mathrm{m^3\,h^{-1}}$ corresponding to a cross-flow velocity close to $0.1\,\mathrm{m\,s^{-1}}$.

After RO of (un)modified skim milks and careful water rinsing, the spiral membrane is cleaned 1 h at 50°C under 10 bar with an alkaline formulated detergent (P3-Ultrasil 10, Ecolab) at 0.4 wt.% (natural pH = 12.0). Cleaning step is performed in similar hydrodynamic conditions as fouling: VRR = 1 and $0.8\,\mathrm{m^3\,h^{-1}}$. This cleaning step is efficient, regardless of the pH of the modified skim milk, except for pH lower than 4.0. Calcium phosphate precipitation occurs at very acidic pH. It severely fouls the membrane. In such conditions, an acid cleaning step with HNO_3 (pH 1.6) is needed to restore the initial membrane flux. The recovery of water flux is always better than 90%, meaning that the hydraulic cleanliness is systematically obtained.

The performance of RO is expressed as observed retention (Ret) of lactose, proteins or COD according to Eq. (1).

$$\mathrm{Ret}\ (\%) = 100 \times (1 - C_p/C_b) \qquad (1)$$

where C_p is the concentration in the permeate and C_b is the concentration in the bulk.

The concentration of lactose is determined by the Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) at 1,041 cm^{-1} (C–O ether bond) with a Paragon 1,000 spectrometer (Perkin Elmer); this method is adapted from classical near IR analyser. The spectrometer is equipped with an ATR ZnSe crystal with a nominal incident angle of 45° allowing 25 reflections. Spectra are acquired from 20 scans with a resolution of 2 cm^{-1} and a background registered in the air. Protein concentrations are similarly determined, but at a wavenumber of 1,540 cm^{-1} (amide II bond). In both cases, the precision is better than 5%.

The COD is measured with a 160 COD kit (Macherey Nagel) after appropriate dilution of the sample with a precision at ca. 5%. Finally, for all types of analyses, the precisions on retention are better than 10%.

2.3. RO: critical flux, limiting flux and flux decline origin calculation

During solute filtration, TMP increase leads to increase of permeate flux (J). The plot of J vs. TMP is linear below the critical point (J_{critical}, $\text{TMP}_{\text{critical}}$), delimiting the critical conditions of filtration. Beyond a given minimum pressure, further called the limiting TMP ($\text{TMP}_{\text{limit}}$) the flux does not increase anymore and a constant maximal value corresponding to the limiting flux (J_{limiting}) is reached. Both fluxes are determined from Fig. 1 and similar ones with a precision close to 5% by increasing step by step the TMP with a given fluid. Each increase of TMP is realised after a plateau value of flux is reached during the previous pressure step.

The followed procedure is validated as it is verified that after reaching the limiting flux plateau value, a progressive decrease of TMP evidences the occurrence of a hysteresis of flux (not shown).

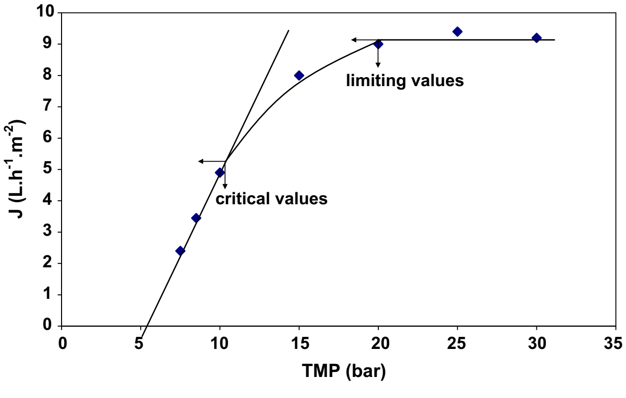

Fig. 1. J flux vs. TMP at pH 6.7 and 25°C to explain limiting and critical point experimental determination.

The fouling evaluation is also described thanks to the model of resistance in series that is generally satisfactory for food fluids. Darcy's law is modified as follows:

$$J = \text{PTM} \times 1/(R_{\text{tot}} \times \eta) \quad (2)$$

$$R_{\text{tot}} = R_{\text{m}} + R_{\text{f}} \quad (3)$$

$$R_{\text{f}} = R_{\text{reversible}} + R_{\text{irreversible}} \quad (4)$$

where R_{tot} is the total resistance to solvent transfer; R_{m} is the hydraulic resistance of the clean/pristine membrane; R_{f} is the hydraulic resistance of global fouling; $R_{\text{reversible}}$ is the hydraulic resistance of reversible fouling, corresponding to polarisation concentration but also in this case to the reversible part of a gel, the formation of which is due to proteins. The removal of the reversible part of the gel is evidenced, for instance, in UF when filtration is performed in transparency plate and frame module. This part of fouling is easily removed by water rinsing. $R_{\text{irreversible}}$ is the hydraulic resistance of irreversible fouling, corresponding to severe fouling strongly attached to the membrane and perhaps including the irreversible part (if any) of the gel mentioned above. This part of fouling is not removed by water rinsing and chemical cleaning is needed.

Moreover, applying this model two particular fouling resistances are introduced, further called $R_{\text{irrev,limiting}}$ and $R_{\text{f,sub-critical}}$.

$R_{\text{irrev,limiting}}$ corresponds to the irreversible fouling obtained at the end of filtration experiments achieved up to the limiting flux at 30 bar, that is, a sufficient TMP to reach the limiting fluxes for all experiments with natural and un-diluted modified skim milks.

$R_{\text{f,sub-critical}}$ corresponds to the average fouling resistance obtained for filtration in sub-critical conditions (determined from the apparent permeability in sub-critical conditions calculated from the slope of J vs. TMP in Fig. 1).

As small salts are retained by the RO membrane, the effective pressure is the applied TMP minus the osmotic pressure difference between the retentate and the permeate sides. The osmotic pressure of milk is close to 7 bar, roughly equally due to lactose and salts contributions and without significant influence of proteins. From a practical point of view, the difference in osmotic pressure ($\Delta\pi_0$) can be easily determined from extrapolation at $J = 0$ on the plot of J vs. TMP (Fig. 2). Thanks to the fact that salt retention is roughly constant with TMP for a given pH, we then considered

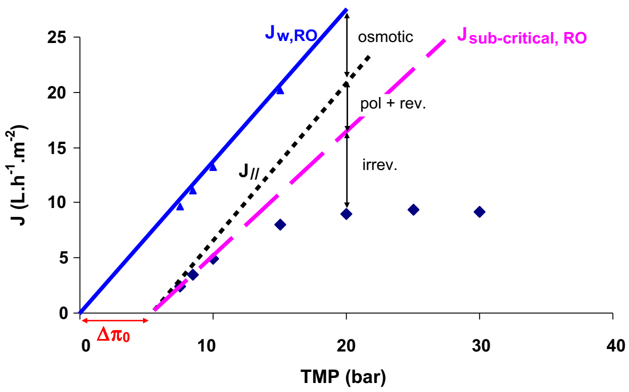

Fig. 2. Principle of calculation of flux decrease during RO of natural or modified skim milks (see Appendix A for equations). Results in the figure correspond to the case of RO of natural un-diluted skim milk (pH 6.7). ▲: water flux of the pristine/clean membrane ($J_{w,RO}$) ♦: flux in natural skim milk ($J_{milk,RO}$). ……. the straight line is parallel to the water flux, but intercepts x axis at TMP = $\Delta\pi_0$ ($J_{//}$) ---- the straight line follows the straight part of the curve of the flux in natural skim milk that is located below $J_{critical}$ but is not parallel to water flux ($J_{sub\text{-}critical,RO}$).

that difference in osmotic pressure is constant and equal to $\Delta\pi_0$ regardless of the TMP.

Fig. 2 shows the calculation steps given in detail in Appendix A. During RO of (un)modified skim milk, the flux decrease (when compared to water flux of the pristine/clean membrane) is decomposed according to its origin:

(i) The decrease of flux due to osmotic effect is further called $\Delta J_{osmotic}$.
(ii) The decrease of flux due to reversible accumulation of fluid at the membrane wall, further called $\Delta J_{pol+rev}$, is due to concentration polarisation and partly to gel formation (reversible part of the gel). Besides the effects of osmotic pressure, these phenomena are responsible for whole reduction of flux as long as no irreversible deposit fouled the membrane, so when J is lower than $J_{critical}$.
(iii) The irreversible fouling deposit exists only for flux greater than the critical flux, leading to determine flux decrease as ΔJ_{irrev}.

3. Results and discussion

3.1. Retentions vs. pH of natural and un-diluted modified skim milks.

The proteins and lactose retentions are similar at both limiting and critical fluxes and always greater than 99.9% in the considered pH range from 3.5 to 11.5. The COD of retentate corresponds mainly to proteins and lactose (citrate has a negligible contribution compared to the others). Only lactose (and few citrates, no fermentation of lactose leading to lactic acid with fresh solutions used in this case) is able to cross the membrane towards the permeate side and thus to contribute to the COD of permeate. Finally, the retention of COD is greater than 99.9%, regardless of the pH and the flux; it is generally sufficient to consider requirements (120–125 mg L^{-1}) for discarding in natural media (Fig. 3).

The retention of total salts varies with the pH, but the conductivity of permeate is always lower than the standard of drinking water (fixed at 1,000 µS cm^{-1} considered as reference, as there is no standard for effluent rejection) (Fig. 4).

The retentions are affected by the RO conditions and are always slightly better at limiting flux than at critical flux. As dissociation equilibrium in milk is strongly modified with the pH, thus the amount of free salts (not bounded to proteins) present in the feeds to be filtered very strongly. Moreover, especially for calcium, phosphate and citrate, the chemical form changes for free ions at acidic pH to soluble chelated ones at alkaline pH. The whole salts content, in solution, is lower at natural pH of milk (6.6–6.7) corresponding logically to the lower conductivity in the RO permeate. For other pHs, demineralisation of casein micelles is the most important factor for extreme pHs (acidic and alkaline ones) and logically leads to a higher conductivity in the RO permeate.

Finally, critical and limiting RO filtration conditions lead more or less to acceptable COD and conductivity in the permeate. Modelling concentrated dairy effluents (natural and un-diluted modified skim milks) and considering on a strictly productivity point

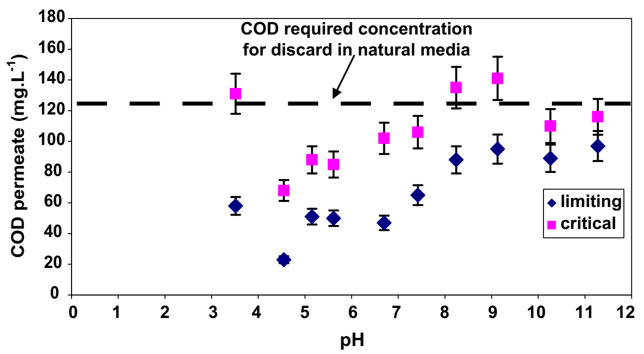

Fig. 3. COD of permeates vs. pH of natural and un-diluted modified skim milks for RO performed at limiting and critical fluxes. The COD required concentration was fixed at 125 mg L^{-1} in the figure.

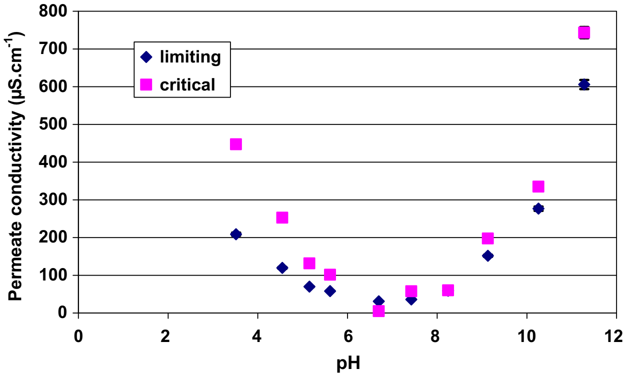

Fig. 4. Permeate conductivity vs. pH of natural and un-diluted modified skim milks when RO was performed at limiting and critical fluxes—error bars are generally greater than the point symbols—standard for drinking water is 1,000 µS cm^{-1}.

of view the sole effluent treatment step by RO, fluxes management would be the main parameter for the choice of RO conditions. Nevertheless, the cleaning-in-place procedure must also be taken into account.

3.2. TMP and osmotic pressure vs. pH of natural and un-diluted modified skim milks

The critical TMP (close to 10 bar) and limiting one (close to 20 bar) are constant in the pH range 3.5–10.0 (Fig. 5). Roughly, $\Delta\pi_0$ is close to $\Delta\pi_0 = 4.8 \pm 0.9$ bar (20% variation), except for pH 9 that seems to be a particular pH in this system (Fig. 6).

As already explained, $\Delta\pi_0$ mainly depends on lactose and soluble minerals. The roughly constant retention of lactose with pH and flux leads to about 3 bar contribution to $\Delta\pi_0$. The amount and the chemical nature of dissolved salts change with the pH (free ions, chelated ions, leakage of ions bounded to caseins and other proteins) and thus the contribution of the soluble mineral fraction to the behaviour of $\Delta\pi_0$ vs. pH is difficult to comment. Surprisingly, $\Delta\pi_0$ variation does not influence both critical and limiting TMP in the pH range 3.5–9.5.

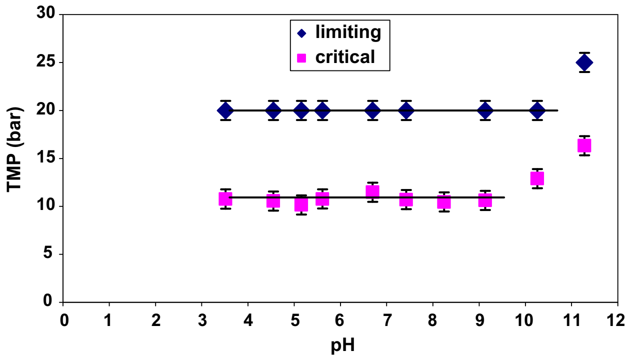

Fig. 5. Limiting and critical pressures vs. pH of natural and un-diluted modified skim milks.

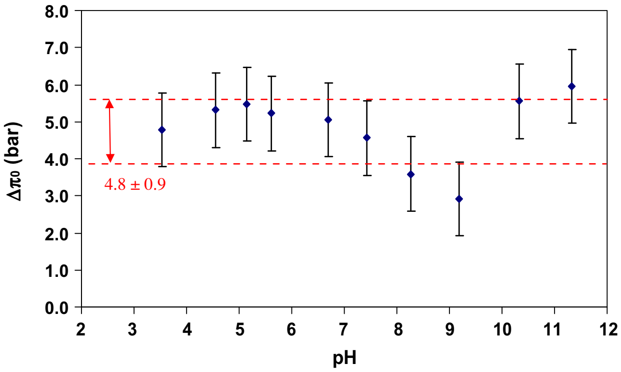

Fig. 6. Variation of $\Delta\pi_0$ vs. pH of natural and un-diluted modified skim milks.

3.3. Hydraulic resistances of fouling vs. pH of natural and un-diluted modified skim milks

The initial permeability to water of the membrane is $Lp_{w,RO} = 1.49 \pm 0.08\ \mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$. In natural and

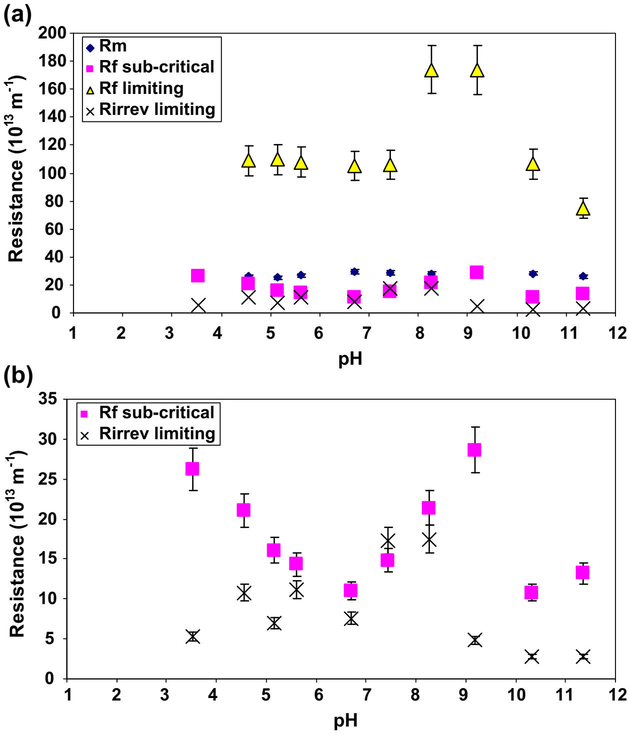

Fig. 7. RO of natural and un-diluted modified skim milks vs. pH. (a) Whole vision (b) zoom. R_m = resistance of clean/pristine membrane; $R_{f,\text{sub-critical}}$ = resistance of fouling in sub-critical region; $R_{f,\text{limiting}}$ = resistance of whole fouling at final limiting flux at 20 bar; $R_{\text{irrev, limiting}}$ = resistance due to irreversible fouling at final limiting flux at 20 bar.

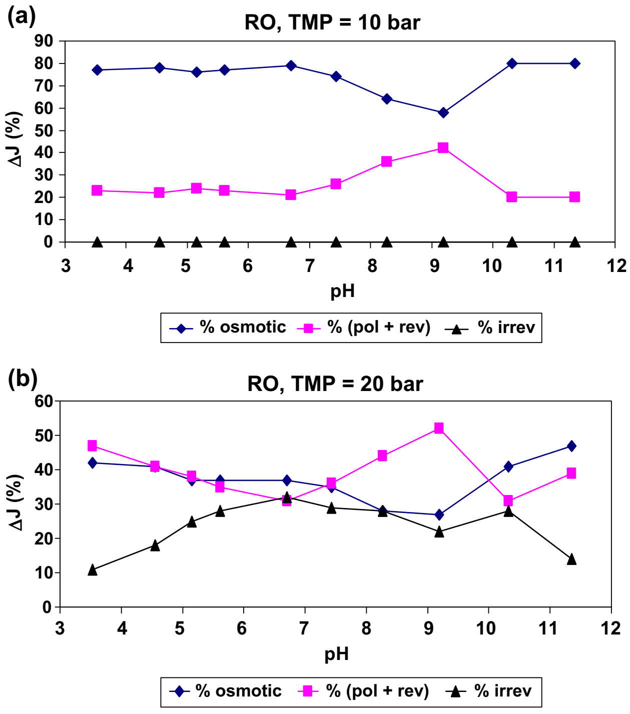

Fig. 8. The effect of pH on flux proportion losses during natural and un-diluted modified skim milk RO (a) in critical conditions (10 bar) and (b) in limiting conditions (20 bar).

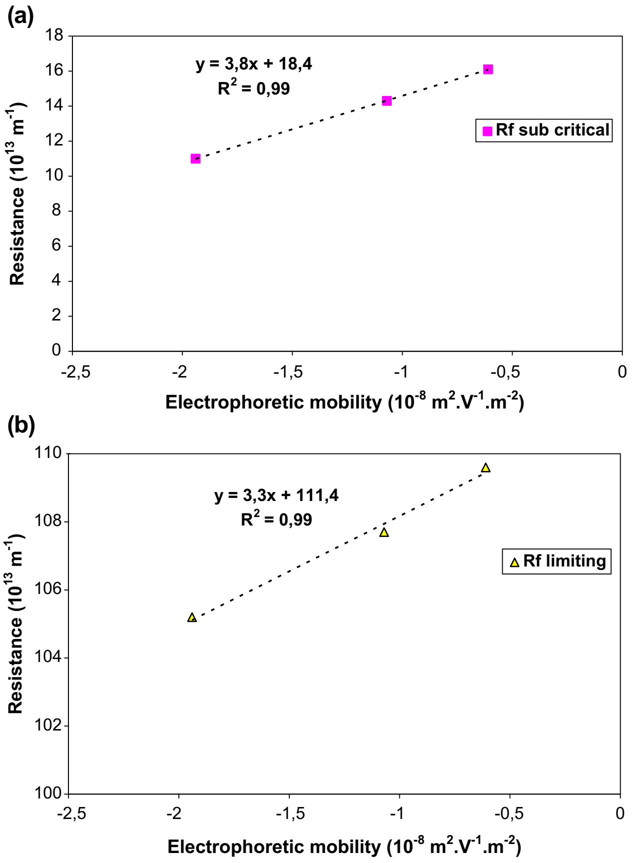

Fig. 9. Variation of (a) $R_{f,sub\text{-}critical}$ and (b) $R_{f,limiting}$ vs. electrophoretic mobility of caseins in the pH range 4.5–6.7 where casein size was constant and close to 210 nm.

un-diluted modified skim milks, the permeability in sub-critical conditions is relatively constant with the pH ($Lp_{sub\text{-}critical,RO} = 0.9 \pm 0.1\ \mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$, 13% variation) and evidences a weak-like form of all the J vs. TMP curves. This form suggests the build-up of a reversible fouling (reversible part of the gel) and/or the existence of concentration polarisation at lower fluxes.

Variation of hydraulic resistances inferred from fluxes variation is given in Fig. 7.

Of course, thanks to the resistance in series equation, the whole fouling resistance (R_f) varies vs. pH inversely as flux variation. The behaviour of the irreversible fouling at final TMP (20 bar), $R_{irrev,limiting}$, is close to that of R_f, but slightly shifted for pH greater than 9. $R_{sub\text{-}critical}$ changes do not look the same with pH than the other two previous resistances. Then it can be drawn that the mastering of these different resistances is not due to the same components.

Details of flux reduction due to osmotic effect, reversible fouling and polarisation concentration as well as irreversible fouling are calculated for two TMP. One is set at 10 bar representative of sub-critical conditions and the other at 20 bar representative of limiting conditions (Fig. 8). In sub-critical conditions of RO, the limitation of flux is clearly mainly due to osmotic effects, regardless of the pH. In limiting conditions, the decrease of flux is roughly equally shared between the three possible origins.

3.4. Chemical components' possible impact on fouling at acidic pH

For pH ranging between 4.5 and 6.7, the size of caseins is roughly constant and similar to that of native micelles (210 nm), while the electrophoretic mobility strongly vary between -0.3×10^{-8} and $-1.9 \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$. Resistance in sub-critical conditions ($R_{f,sub\text{-}critical}$) and limiting conditions ($R_{f,limiting}$) is plotted against the caseins' electrophoretic mobility (charge) suggesting linear tendencies (Fig. 9) evidencing that the resistances increase when the casein net charge decreases. Then it can be drawn that repulsive electrostatic interactions involving caseins play a role on the apparent porosity of the whole fouling. According to the critical flux concept, the main difference between these two resistances would be the builtup of the irreversible deposit layer, but as shown,

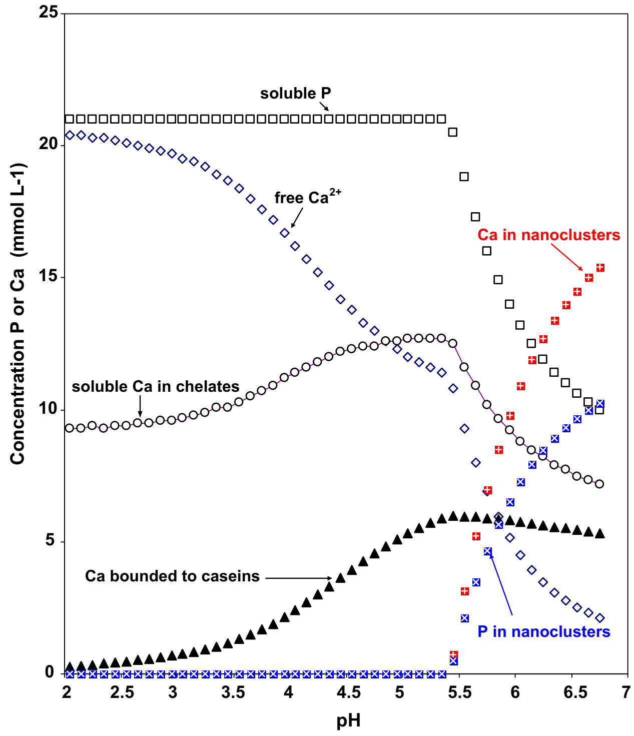

Fig. 10. Various forms of calcium and phosphorus vs. pH in natural and un-diluted modified skim milks as calculated from MILKSALT software.

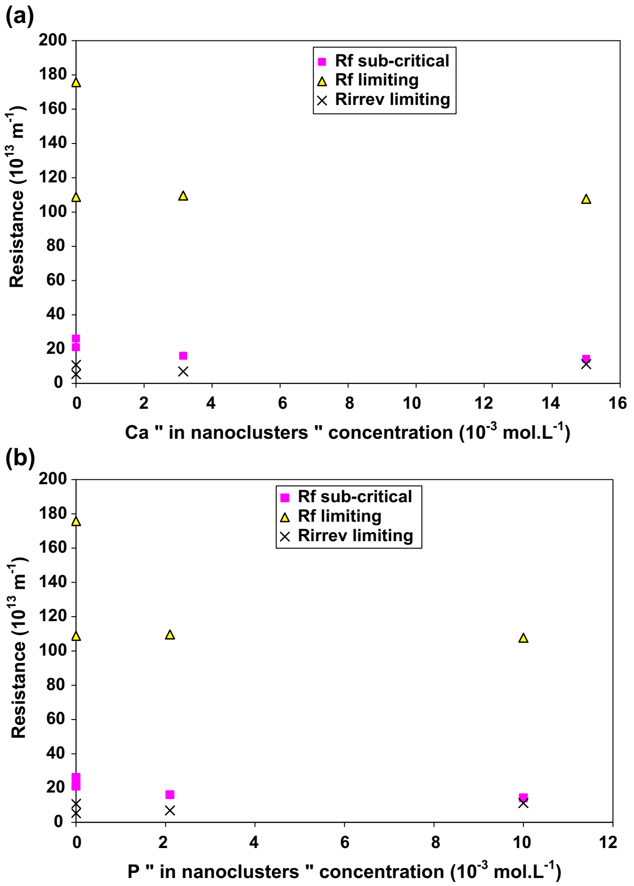

Fig. 11. Variation of fouling resistances during RO of natural and un-diluted modified skim milks in the pH range 3.5–6.7 vs. (a) calcium in nanoclusters stabilising casein micelles and (b) phosphate in nano-clusters stabilising casein micelles.

Fig. 7(b), the resistance due to the irreversible fouling is rather constant in this pH range and thus appears not solely due to caseins.

Thus, the possible role of inorganic components on the fouling behaviour must be discussed. Thanks to the ability to move from free salts to soluble chelates and/or to precipitates in the considered pH range, focus on calcium and phosphate is done. They are commonly considered (generally from membrane autopsy) as the two main inorganic components entering the inorganic fouling (if any). The other salts have not been considered.

As calcium phosphate, in nanocluster form, stabilises the casein micelles, its role is not easily distinguished from that of caseins themselves. It is quite well known that the micelles destabilisation at acidic pH is classically associated to the leakage of both phosphate and calcium. Then the amount of both soluble calcium and phosphate increases in the aqueous phase of modified skim milks and leads to an increase in fouling.

Then attempts have been done to correlate irreversible fouling to the soluble mineral fraction (free from proteins) in the natural and modified un-diluted skim milks in the pH range 3.5–6.7 for which repartition of different forms of calcium, phosphate and citrate can be calculated from the MILKSALT software developed at STLO-INRA Rennes (see [7] and reference cited herein). For the sake of clarity, Fig. 10 shows the various forms of calcium and phosphorus vs. pH in acidic conditions. Except nanoclusters of phosphate and calcium existing only in the pH range 5.5–6.7, all other forms coexist in the whole pH range 2.0–6.7, but in different proportions.

As general trends, the whole fouling resistance increased with the soluble calcium and phosphate increase and particularly with the free Ca^{2+} amount (Figs. 11 and 12).

4. Conclusion

The objective of this work is to study the RO of a complex medium: natural or modified undiluted skim milk in order to model transient dairy effluents, approximately 20 times concentrated.

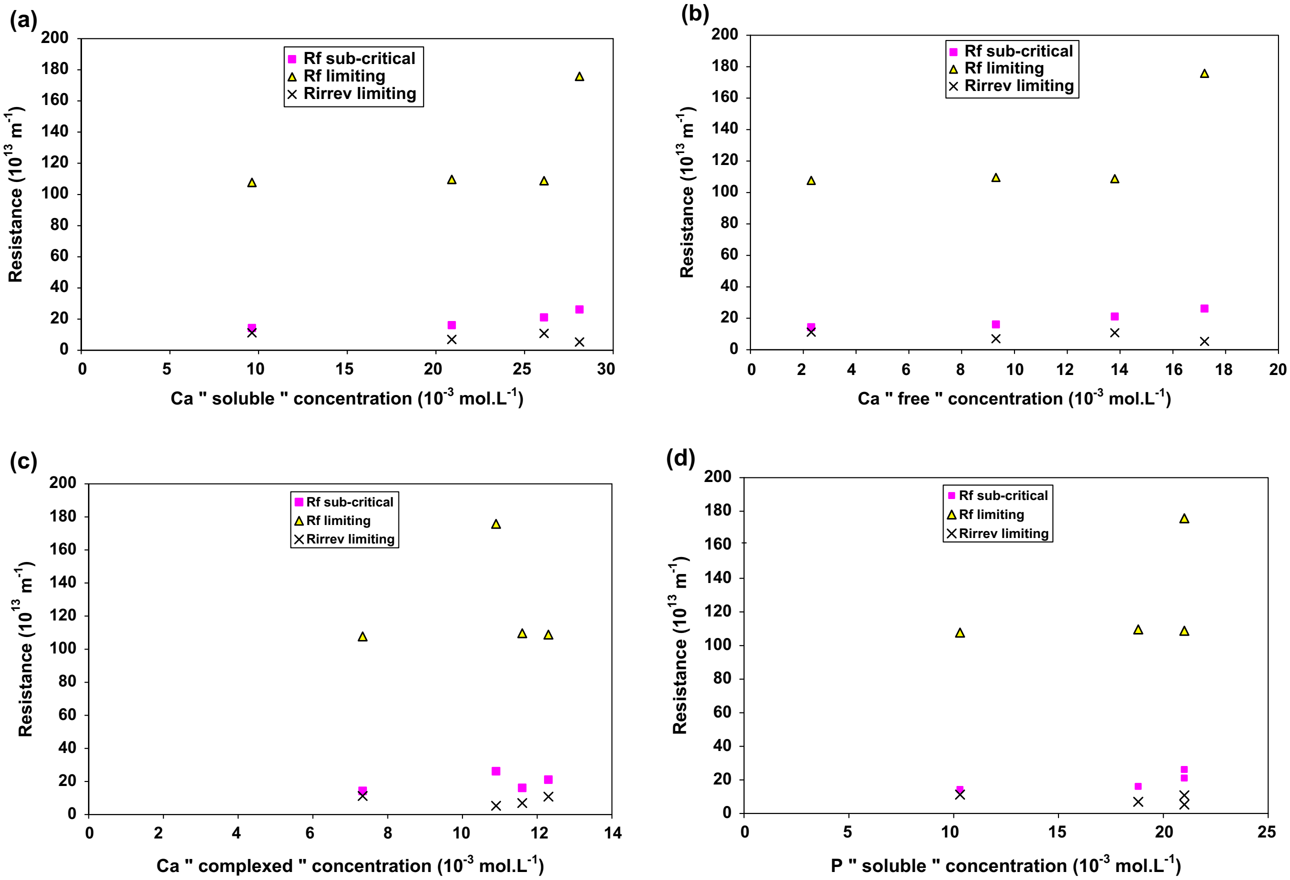

Fig. 12. Variation of resistances of RO filtration of natural and un-diluted modified skim milks in the pH range 3.5–6.7 vs. (a) whole soluble calcium concentration, (b) free calcium (Ca^{2+}) concentration, (c) concentration of calcium in complexed forms (cumulative value of citrate and phosphate chelates), (d) whole soluble phosphate concentration.

As expected, the COD retention is almost total in RO (99.9%), regardless of the pH and the flux, either critical or limiting one. Consequently, the irreversible deposit which is additionally built up between these two "extreme" fluxes has a low impact on the retention of organic components that seemed mainly controlled by the part of the fouling layer closely attached to the membrane. Variation of permeate conductivity appears mainly due to variation in salt composition with pH.

An in-depth analysis of origin of flux decrease highlighted the major role of osmotic effects at lower fluxes (sub-critical conditions) and equally shared effects of osmotic pressure, irreversible fouling and other reversible phenomena (concentration polarisation and gel) at higher fluxes (limiting conditions). Fouling resistances appear correlated to casein micelles deposit, but the fouling resistance also increases with the calcium-and phosphate-soluble fractions in modified skim milks. The free soluble calcium appears as the main promoter of the mineral fouling in/on the membrane. These results are in good agreement with those of previous studies considering only a slight variation of skim milk at pH close to that of natural milk [8–10].

Such results can help to appreciate the best conditions for a good productivity of effluent treatment by membrane processes. Considering cleaning requirement of the RO membrane, no problems are evidenced for neutral (effluents separated at source) and alkaline (whole effluents or transient effluents issued from alkaline cleaning steps) modified milks and a single alkaline cleaning step of the RO membrane is sufficient. On the contrary, RO treatment of acidic transient effluents (issued from acidic cleaning steps) must be avoided as acidic pHs lead to severe inorganic fouling of membrane by calcium phosphate and thus an additional acid cleaning step must be added to the alkaline one. Moreover, the efficiency of the acid cleaning step is strongly dependent on the effluent pH.

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Appendix A: Calculation of flux decline origin

The water flux of the clean membrane was classically determined from:

$$J_{\mathrm{w,RO}} = \mathrm{Lp}_{\mathrm{w,RO}} \times \mathrm{TMP} \tag{5}$$

where $J_{\mathrm{W,RO}}$ is the water flux of the clean membrane and $\mathrm{Lp}_{\mathrm{W,RO}}$ is the membrane permeability to water.

The difference in osmotic pressure ($\Delta\pi_0$) was determined from the J vs. TMP experimental curve by extrapolation of the linear part in the sub-critical region and corresponds to TMP at J equal to zero.

$$J_{\text{sub-critical,RO}} = \mathrm{Lp}_{\text{sub-critical,RO}} \times (\mathrm{TMP} - \Delta\pi_0) \tag{6}$$

where $J_{\text{sub-critical,RO}}$ is the flux in modified milk in the sub-critical region and $\mathrm{Lp}_{\text{sub-critical,RO}}$ is the membrane permeability in the sub-critical region.

Eq. (A3) corresponded to the straight line parallel to that of the water flux and intercepting x-axis at $\Delta\pi_0$:

$$J_{//} = \mathrm{Lp}_{\mathrm{w,RO}} \times (\mathrm{TMP} - \Delta\pi_0) \tag{7}$$

where $J_{//}$ is the calculated flux parallel to water flux but intercepting TMP axis at $\Delta\pi_0$.

The decrease of flux by reversible accumulation of fluid at the membrane wall was due to concentration polarisation and gel formation (due to proteins that we observed experimentally in a transparent plate and frame modules during the UF of skim milk). These gels were easily removed during the water rinsing after filtration. Besides the effects of osmotic pressure, these phenomena were responsible for major reduction of flux as long as no irreversible deposit fouled the membrane. The flux decrease was determined from a comparison between the water flux and the experimental flux in natural or modified undiluted skim milk. Moreover, it was considered that the irreversible fouling deposit existed only for flux greater than the critical flux. Finally, for a given TMP, the origin of loss of the filtering flux was estimated in the following way:

$$\Delta J_{\mathrm{osmotic}} = J_{\mathrm{w,RO}} - J_{//} \tag{8}$$

$$\Delta \mathrm{J}_{\mathrm{pol+rev}} = \mathrm{J}_{//} - \mathrm{J}_{\text{sub-critical,RO}} \tag{9}$$

$$\Delta \mathrm{J}_{\mathrm{irrev}} = \mathrm{J}_{\text{sub-critical,RO}} - \mathrm{J}_{\mathrm{milk,RO}} \tag{10}$$

where $J_{\mathrm{milk,RO}}$ is the flux of the membrane in the natural or modified skim milk at the considered TMP; $\Delta J_{\mathrm{osmotic}}$ is the loss related to the osmotic pressure; $\Delta J_{\mathrm{pol+rev}}$ is the loss related to the concentration polarization and reversible fouling; $\Delta J_{\mathrm{irrev}}$ is the loss related to irreversible fouling deposit.

Accordingly, the flux proportions losses were calculated in the following way,

$$\%\,\Delta J_{\mathrm{osmotic}} = 100 \times \Delta J_{\mathrm{osmotic}} / (\Delta J_{\mathrm{osmotic}} + \Delta J_{\mathrm{pol+rev}} + \Delta J_{\mathrm{irrev}}) \tag{11}$$

$$\%\,\Delta J_{\mathrm{pol+rev}} = 100 \times \Delta J_{\mathrm{pol+rev}} / (\Delta J_{\mathrm{osmotic}} + \Delta J_{\mathrm{pol+rev}} + \Delta J_{\mathrm{irrev}}) \tag{12}$$

$$\%\,\Delta J_{\mathrm{irrev}} = 100 \times \Delta J_{\mathrm{irrev}} / (\Delta J_{\mathrm{osmotic}} + \Delta J_{\mathrm{pol+rev}} + \Delta J_{\mathrm{irrev}}) \tag{13}$$

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