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Implementation of integrated membrane processes for pilot scale development of fractionated milk components

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Abstract — Numerous opportunities for the separation and fractionation of milk and whey components are presented as a result of continuing developments in filtration membranes modules and processes. The preparation of sufficient quantities of selected protein groups for functionality studies and food application tests requires considerable amounts of starting material, particularly in the case of whey-based constituents. Adequate amounts of membrane filtration surface area are, therefore, needed in order to expedite processing time, limit conditions for microbial growth and increase productivity from a product development point of view. With this objective in mind, a series of large pilot plant membrane separation systems based on microfiltration, ultrafiltration and electrodialysis were recently installed and commissioned. Rapid ultrafiltration of whey for the generation of high protein concentrates under a wide variety of conditions, including 'cold' filtration, is facilitated by a Memtech™ spiral wound membrane plant with a maximum surface area of 144 m^2 that is accommodated within 3 modules mounted in parallel. Designed to operate on a continuous feed-and-bleed principle, product is heated while pumping via a plate-heater to the plant's balance tank in order to raise temperature to the desired operating condition. Magnetic flow meters mounted on the feed, permeate and diafiltration water lines enable the volume concentration ratio to be controlled throughout a run. Defatting of rennet whey by microfiltration using a Tetra Pak Alcross™ M, Type 2 × 19 Special, crossflow microfiltration (MF) plant fitted with a 0.1 μm pore size ceramic membrane with a filtration area of 13.3 m^2 trebled flux rate during ultrafiltration at 12 °C under steady state conditions. High protein whey protein concentrates (ca. 80% total protein) were processed in the defatted and non-defatted state at either 50 °C or 12°C for functional characterisation. Preliminary analyses indicate that all 4 WPC's produced weak gels. Native phosphocasein was prepared from skim milk using the above MF plant. Partial demineralisation of skim milk prior to MF was facilitated using an Ionics (Ionics Inc.) Electromat™ ED, featuring a 100-cell pair Mark III electrodialysis membrane stack. Electrodialysis resulted in improvements in the heat stability profile of phosphocasein, at the expense of rennet coagulation properties which were totally eliminated even in the presence of added calcium.

'cold' whey ultrafiltration / whey protein concentrate / phosphocasein

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1. INTRODUCTION

Numerous opportunities for the separation and fractionation of milk and whey components are currently achievable as a result of continuing developments in filtration membranes, modules and processes [13, 14].

Spiral wound membrane-based ultrafiltration (UF) systems are now universally adopted as a first choice for industrial protein separation. The compact nature of this type of membrane lowers initial investment costs, and makes less demands on space requirements within the processing environment. The availability of a wide range of UF membranes on the basis of molecular weight cut-off enables fractionation of protein mixtures ranging from immunoglobulins to small peptides.

Crossflow microfiltration (MF) technology using ceramic membranes is now industrially applied for the 'clean-up' of protein systems such as defatting and the removal of microparticulate material. Further UF processing of defatted wheys facilitates the preparation of whey protein concentrates (WPC's) in 'isolate' forms. Functionality [17] as exemplified by foaming properties and flavour [4] are improved as a result of removing the residual lipid content of whey. Crossflow MF is also proving to be a valuable tool in preferentially separating protein micelles from other soluble forms present to produce native phosphocasein in an enriched form. The original work of Fauquant et al. [3] on native casein separation, based on the MF principles underlying the Bactocatch™ procedure, has been developed through further studies based on spray dried, diafiltered, MF phosphocasein retentate [20]. The resulting enriched micellar caseinate is close in protein composition to commercial calcium caseinate powder. It exhibits reduced rennet clotting time and increased gel development kinetics [18]. These powders are suitable for the standardisation of milk in cheesemaking processes by increasing the protein concentration without increasing the lactose content.

The aim of this study was to specify and commission a complementary range of pilot scale membrane separation processes in order to expand the Centre's capability in terms of process development and protein functionality, and have sufficient process capacity in order to integrate with existing evaporation and spray drying facilities (water evaporation rates of 900 $L \cdot h^{-1}$ and 100 $L \cdot h^{-1}$, respectively). A particular objective was to produce WPC's under 'cold' (< 20 °C) processing conditions in order to determine the effects on plant performance and protein functionality in the light of recent work by Britten and Pouliot [1] who showed that structural alteration of β-lactoglobulin as a result of processing was evident in cheese WPC (779 $g \cdot kg^{-1}$ protein in dry matter) and to a lesser extent in whey protein isolate (958 $g \cdot kg^{-1}$ protein in dry matter) prepared from milk MF permeate. These authors were of the opinion that prolonged batch concentration and pumping at 50 °C during UF using a hollow fibre membrane plant with inlet and outlet pressures of 1.8 and 0.6 bar, respectively had a negative effect on protein structure. In current study, the results of initial plant performance tests conducted during the preparation of (i) WPC's (defatted and non-defatted) under standard and 'cold' temperature processing conditions and (ii) native phosphocasein are examined.

2. MATERIALS AND METHODS

The experimental plan for the preparation of WPC's and native phosphocasein (Fig. 1) was executed on the following membrane processes that were installed and commissioned at the end of 1998.

2.1. Membrane process

2.1.1. Microfiltration

Whey defatting either from fresh starting material or partially concentrated UF retentate is optional using a Tetra Pak (Tetra

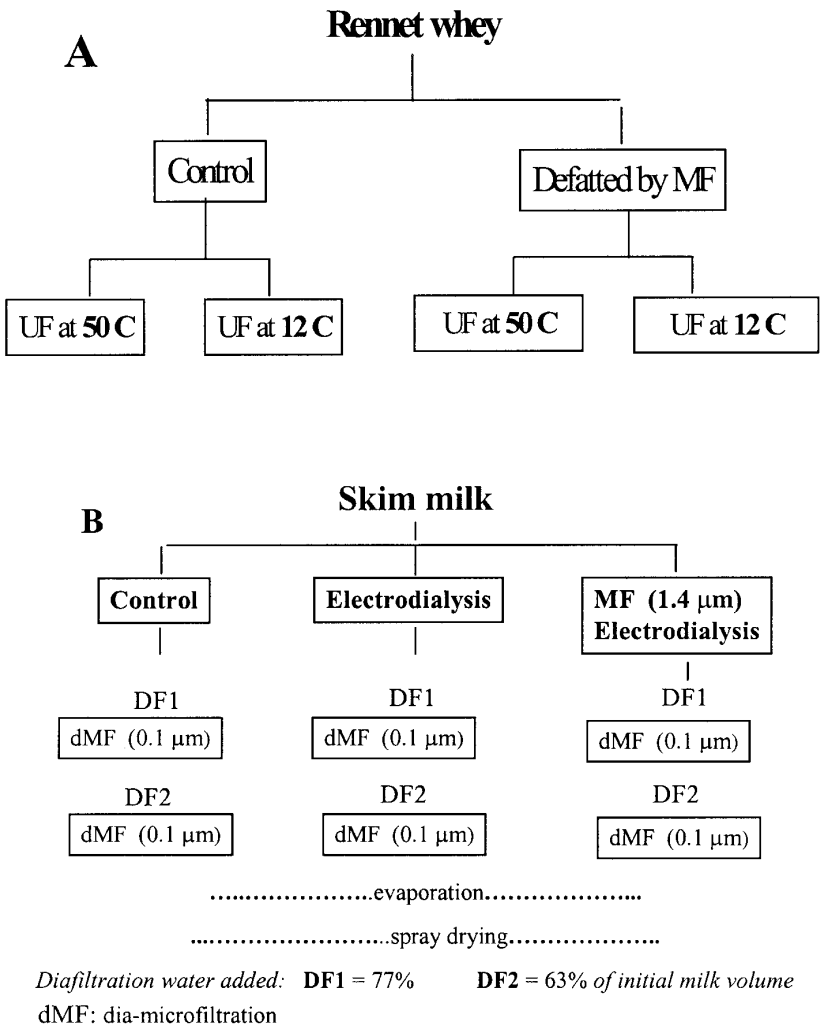

Figure 1. Experimental design for the preparation of (A) whey protein concentrates, and (B) native phosphocasein.

Pak Filtration Systems, Aarhus, Denmark) Alcross™ M, Type 2 × 19 Special, cross-flow microfiltration plant fitted with a 0.1 μm pore size MEMBRALOX™ ceramic membrane with a filtration area of 13.3 m^2. This plant with its 2 membrane modules mounted parallel is also fitted on one of the loops, through flexible interconnections, with a single 1.4 μm pore size MEMBRALOX™ ceramic MF module with a filtration area of 6.65 m^2. Changeover to bacteria removal duties by MF is, therefore, readily facilitated by readjustment of the plant's pre-set flow rates.

The plant was operated according to the Uniform Transmembrane Pressure (UTMP) principle devised by Tetra Pak with process settings being generally established during start-up on water in order to maintain an UTMP differential of approximately 0.3 bar.

2.1.2. Demineralisation

An Ionics (Ionics Inc, Watertown, Mass, USA) Electromat™ ED, featuring a 100-cell pair Mark III electrodialysis membrane stack, and which is capable of handling whey from raw as well as concentrated (evaporated; membrane retentates) sources was used for partial demineralisation of skim milk.

2.1.3. Ultrafiltration

A Memtech (Memtech Ltd, Swansea, UK) spiral wound (molecular weight cut-off = 5 kg·mol^{-1}) membrane plant with a maximum surface area of 144 m^2, accommodated within 3 parallel mounted filtration modules was installed for ultrafiltration of whey and skim milk. Designed to operate on a continuous feed-and-bleed principle, product is fed via an in-line plate heater in order to raise temperature to the desired operating condition. The dead volume, i.e. the amount of liquid required to fill voids associated with pipework, pumps and membrane modules in the plant, totalled 127 L or 0.88 L·m^{-2} membrane area. Magnetic flow meters mounted on the permeate, retentate bleed-off and diafiltration water lines enable the volume concentration ratio to be controlled throughout the run. Process temperature, pressures, permeate and retentate flow rates are captured using an ABB Commander advanced 6-channel recorder fitted with a PCMCIA card that allows data downloading to a personal computer. Additional product input and output data, captured from the digital displays instrumentation associated with load cells attached to the 5 000 L and 10 000 L storage tanks, enhances the monitoring of plant performance.

2.2. Compositional analysis

Total protein was determined according to IDF standard 20B: 1993 [6]; Non-casein nitrogen (NCN) according to IDF standard 29:1964 [7]; Non-protein nitrogen (NPN) according to IDF standard 20B:1993 [6]; moisture content according IDF standard 26A [8]; and fat according to IDF standard 127A:1988 [9]. Ash and phosphorus were measured by AOAC methods 900.02 and 986.24, respectively. Calcium was determined by atomic absorption spectrophotometry.

In addition to the total content of Ca and P, soluble forms of these ions were also measured in ultrafiltrates prepared using an Amicon (Amicon Inc. Gloucestershire, England) stirred cell filtration unit model 202 fitted with PM 10 Diaflo membranes.

2.2.1. Capillary electrophoresis

A Beckmann (Beckman Ltd, High Wycombe, UK) P/ACE capillary electrophoresis, model MDQ, was used to qualitatively identify the major whey protein fractions of whey, whey retentates and WPC according to the method described by Otte et al. [16]

2.2.2. Measurement of zeta potential

The ζ-potentials of phosphocasein micelles were determined using a Malvern Zetamaster (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The ζ-potential of the particles were calculated from Henry's equation [5] $\zeta = 1.5\,\eta\nu/(\varepsilon f(\kappa a))$, where η and ε are respectively the viscosity and dielectric constant of the solution at the temperature of measurement, ν is the electrophoretic mobility of the particle, and f (κa) is 1.5 (a high κa was assumed, since the particles were large). All measurements were made at 20 °C ± 0.5 °C, and the viscosity of the simple buffer systems was taken to be 1.07 at the stated temperature. The dielectric constant was taken as 79.0.

Samples were typically diluted 500 fold using 20 mmol·L^{-1} imidazole, pH 7.0 which included 2 mmol·L^{-1} calcium chloride and 50 mmol·L^{-1} NaCl.

Particle size of the phosphocasein dispersions was determined using the Malvern Zetamaster (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The cumulant method was used to find the mean size (z-average) or the size of a particle that corresponds to the mean of the intensity distribution. All samples were diluted with simulated milk ultrafiltrate SMUF [10] and the viscosity taken as 1.10 mPa·s at 25 °C.

2.3. Functional tests

2.3.1. Gelation

Whey protein concentrates were reconstituted to 10% (w/v) protein solutions, adjusted to pH 7.0 with NaOH, and allowed stand for 30 min. Gels were prepared and tested using an Instron Universal Testing Machine according to modification of the method described by Mulvihill and Kinsella [15]. A portion of the gel, 15 mm high and 14 mm in diameter, was compressed between two parallel plates (150 mm in diameter and 20 mm apart) at a crosshead speed of 10 mm·min^{-1}. The gel was compressed to 20% of its original height followed by further compression to 70% of its original height. The force exerted by the top plate was recorded at each compression. Values represent means of five replicate measurements of each sample.

2.3.2. Heat stability

The heat coagulation time (HCT) of phosphocasein preparations was measured at 4.3% total solids in an oil bath (Elbanton, Kerkdriel, The Netherlands) at 140 °C according to the procedure outlined by Kelly [12].

2.3.3. Rennet clotting characteristics

A Formagraph (Foss Electric A/S, Copenhagen, Denmark) was used to measure the clotting rate as well as gel strength of phosphocasein solutions (10 mL, 4.4% total solids, pH 6.6, inoculated with 77 μL Chymax® (Pfizer Inc. Wisconsin, USA) enzyme, diluted 1/100) prepared in (i) distilled water, (ii) SMUF, and also (iii) SMUF containing supplemented levels of Ca.

2.4. Preparation of whey protein concentrates

Whey with curd fines content < 50 mg·L^{-1} was sourced in two lots of 10 000 L each over a 2-week period from a rennet casein manufacturing plant where it had been pasteurised (72 °C, 15 s) before transport. Both lots were halved approximately for respective ultrafiltration of each half at 50 °C and ~ 12 °C. The second consignment of whey, however, was defatted by microfiltration (using the Tetra Pak Alcross MF plant with a 1.4 μm pore size ceramic membrane as already described) before ultrafiltration.

2.5. Preparation of phosphocaseins

Native phosphocasein was prepared from skim milk by dia-microfiltration, i.e. MF (0.1 μm pore size) at 50 °C of batch-wise diluted skim milk. Diafiltration was initiated at start-up by the addition of 1 000 L warm reverse osmosis (RO) treated water to 1 300 L of preheated (50 °C) skim milk prior to commencement of MF (cf. Sect. 2.1.1.). The ratio between the retentate (phosphocasein) and permeate (whey) phases that were separated continuously during MF was approximately 4:1. A further 800 L RO-water was added to the collected retentate and microfiltered a second time to give a retentate with a total solids (TS) content of 6.3%. After evaporation to ~ 20% TS, a quantity of retentate was spray dried in an Anhydro LAB 3 drier using a 2-fluid atomiser nozzle with air inlet and outlet temperatures of 187 °C and 87 °C, respectively. Expressed in terms of initial skim milk

volume, the amount of diafiltration water (138%) used corresponded generally with the highest level (133%) used by Pierre et al. [18] when maximising the concentration of phosphocasein in dry matter. In contrast, the latter workers added the diafiltration water continuously during MF processing.

The effects of defatting and demineralisation on MF flux rate during phosphocasein separation at 50 °C was studied by subdividing a quantity of skim milk into two batches. Preparatory treatments of both lots involved in one case (i) partial demineralisation by electrodialysis, while the other (ii) was further defatted by MF using a 1.4 μm pore size membrane before partial demineralisation. In addition to plant performance indicators, the effects of these treatments on the composition of some functional properties of the resulting phosphocaseins were also examined. Diafiltration was maintained at the same levels as the control when RO water was added to the following pretreated milks: 500 L RO water added to 650 L electrodialysed skim milk; 410 L RO water added to its retentate and reprocessed by MF; 385 L RO water added to 500 L electrodialysed, MF defatted skim milk; 315 L RO water added to its retentate and reprocessed by MF.

3. RESULTS

3.1. Whey protein concentrates

3.1.1. UF performance – non MF whey

Due to logistical delays, whey pH dropped from a typical value of pH 6.6–6.7, as encountered during rennet casein manufacture, to pH 5.25 by the time UF processing commenced with the first consignment received.

During start-up of UF processing at 50 °C, two-thirds of the membrane capacity (two of three membrane modules) were utilised initially for a 40 min period as it was feared that the in-line heating system may be overloaded. Inlet pressure was then increased from 2.5 to 5.1 bar so that the corresponding transmembrane pressure (TMP) increases were from 1.9 to 3.25 bar, respectively (Fig. 2). A volume reduction ratio of 25:1 was achieved over a 3-hour period as ~ 5 000 L of whey was ultrafiltered using a batch processing mode, i.e. with retentate recirculation to the 300 L feed balance tank of the UF plant until retentate total solids reached 27% TS. UF flux declined steadily throughout the run while feeding whey to reach final values of ~ 7 $L \cdot m^{-2} \cdot h^{-1}$ (Fig. 2A). On termination of the whey feed, diafiltration commenced with the addition, initially, of 200 L RO water. After further concentration, the total retentate content of the UF plant was discharged to a storage tank, where a further 1015 L RO water was added. A cleaning-in-place (CIP) treatment of the membrane plant was carried out, after which diafiltration of the retentate continued until total solids increased to 17.4% TS.

'Cold' UF processing at 12 °C using the second lot (4 141 L) of the same rennet casein whey took approximately 7 h to accomplish (Fig. 2B) in the course of concentrating to a volume reduction ratio of 32:1. A constant feed pressure of 5.1 bar was maintained throughout resulting in a TMP value of 3.9 bar. Flux declined rapidly from an initial 12 $L \cdot m^{-2} \cdot h^{-1}$ to level off at about 5 $L \cdot m^{-2} \cdot h^{-1}$ after 4 h. In this instance, diafiltration water (298 $L \cdot h^{-1}$) was introduced alongside a reduced whey feed rate after 2.1 h so that total solids in the feed tank were maintained relatively steady at 9–11% TS until ~ 5 000 L permeate was collected. After 5.5 h, the whey feed was stopped, and diafiltration water was increased to 850 $L \cdot h^{-1}$ consistent with the permeation rate. On processing for a further 1.25 h, during which time the total solids content in the permeate declined from 4.45% to 0.4%, diafiltration water was closed off and the retentate in the balance tank was concentrated to 22% TS. Total diafiltration water added amounted to 53%. Approximately 300 L retentate at

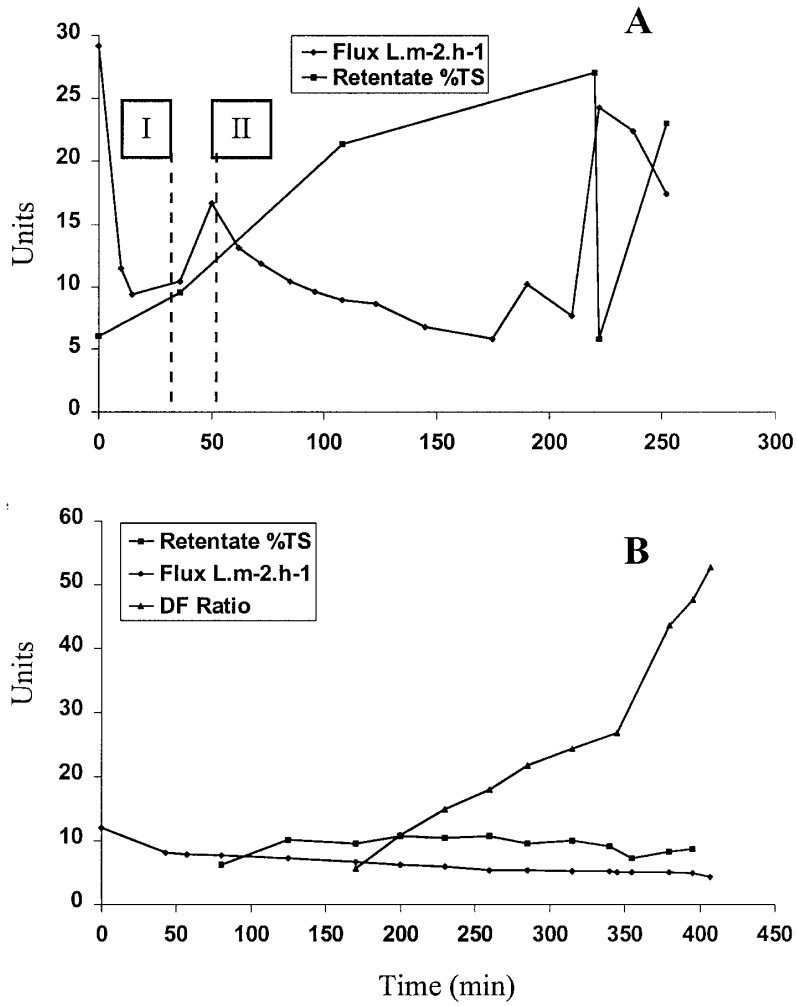

Figure 2. Changes in process parameters during ultrafiltration at (A) 50 °C and (B) 12 °C of rennet whey: flux rate ($L \cdot m^{-2} \cdot h^{-1}$) (◆); retentate % total solids (■); and diafiltration (DF) water ratio (▲); I: membrane area increased from 2 to 3 modules; II: inlet pressure increase to 5.1 bar.

17.5% TS was collected on discharging the contents of the UF the plant.

3.1.2. UF performance – MF defatted whey

Even with the addition of diafiltration water, 4 453 kg of MF defatted whey was concentrated by a factor of 33:1 using UF within 140 min. A permeation rate of 5 733 $L \cdot h^{-1}$ (~ 40 $L \cdot m^{-2} \cdot h^{-1}$) at start-up with MF defatted whey exceeded the whey feed rate to the UF plant for a brief period, and it was necessary to operate initially with an inlet pressure to the membrane of 3.2 bar (TMP = 2.3). A noticeable recovery in flux rate from 24 to 33 $L \cdot m^{-2} \cdot h^{-1}$ was obtained

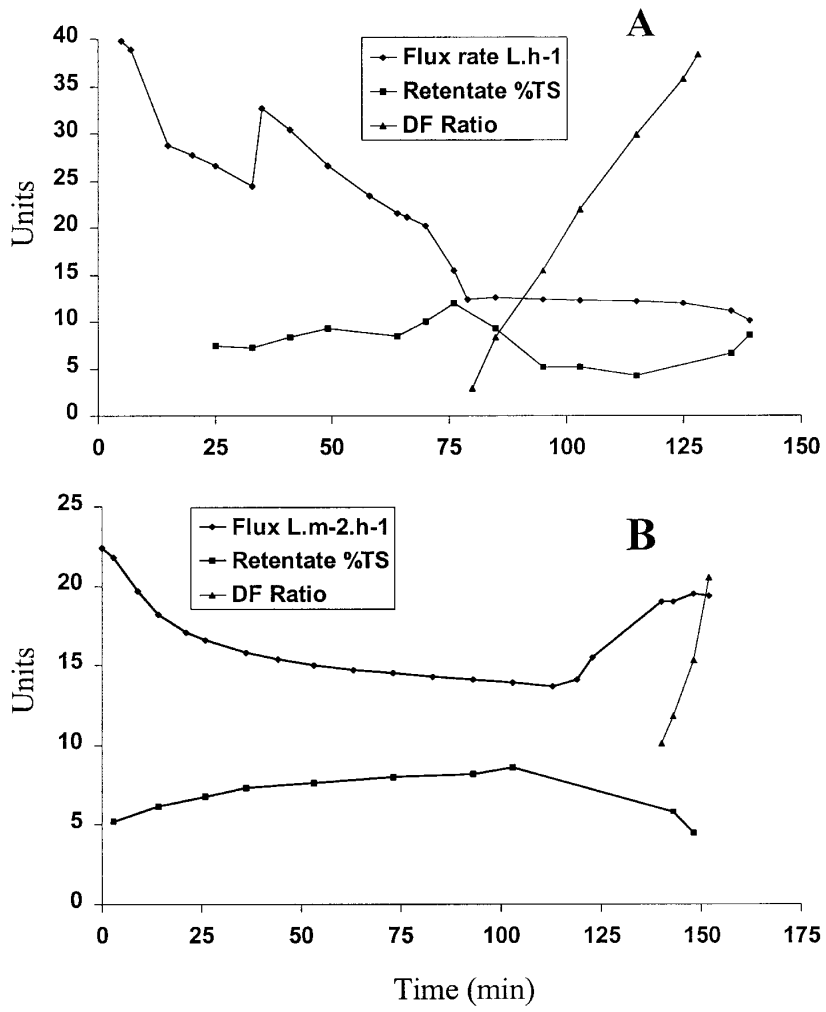

Figure 3. Changes in process parameters during ultrafiltration at (A) 50 °C and (B) 12 °C of MF defatted rennet whey: flux rate ($L \cdot m^{-2} \cdot h^{-1}$) (◆); retentate % total solids (■); and diafiltration (DF) water ratio (▲).

when inlet pressure was increased to 5 bar (TMP = 3.2) at the 35 min processing stage (Fig. 3A). Because of good permeation rates, UF of defatted whey to 12% total solids was accomplished within 70 min before diafiltration commenced. Diafiltration (38%) was then carried out over the following 58 min, according as flux rates fell to a consistent 12 $L \cdot m^{-2} \cdot h^{-1}$ due to temperatures falling to 23 °C since the RO water was unheated. A maximum concentration of the diafiltered retentate to 8.6% total solids could only be achieved at the end of the UF process due to insufficient retentate volume in the plant's balance tank.

Initial flux during UF of MF defatted whey at 12 °C (Fig. 3B) was about half that obtained in the corresponding trial at 50 °C (Fig. 3A). However, the decline during the

first 35 min of operation to 15 $L \cdot m^{-2} \cdot h^{-1}$ – a rate which was sustained throughout the remaining 78 min of the process, suggested that consistent permeation occurred under 'cold' conditions. A total of 5 798 kg of MF defatted whey was concentrated at 12 °C by a factor of 40:1 using a similar TMP value (3.2) as before. Flux recovered to almost 20 $L \cdot m^{-2} \cdot h^{-1}$ during diafiltration and according as temperature increased to 20 °C. Diafiltration in this instance at 20% was the lowest level applied throughout all the trials.

3.1.3. Protein content

The total protein contents of the non-MF defatted, spray dried whey protein concentrates (WPC) processed at 50 °C and 12 °C were 82.19% and 77.90%, respectively. The higher total protein contents of defatted WPC's (89%) suggest these proteins may classified as whey protein isolates.

3.1.4. Gelation

The gelation characteristics of all WPC's produced were poor. The white gels were soft, tended to break easily upon removal from the tubes and especially at an early stage during 70% compression. Displacement at maximum load on the Instron Universal Testing Machine was < 0.5 mm in all cases. Load at Max Load (kgf) was < 0.25 kgf with the exception of the WPC produced at 50 °C from non-MF defatted whey which had a value of 0.54 kgf.

3.1.5. Protein structure effects

Chromatograms prepared by capillary electrophoresis analysis of all samples indicate that there was little or no change in the peak profiles of the major whey protein fractions – β-lactoglobulin and α-lactalbumin. There was some slight evidence of peak enlargement in the case of β-lactoglobulin of the retentate produced from defatted whey by UF at 50 °C. The overall similarity of the peak profiles suggest that little change took place to the structure of whey proteins. This may have been due to the low concentration factors achieved during UF as a result of declining retentate volumes towards the end of processing.

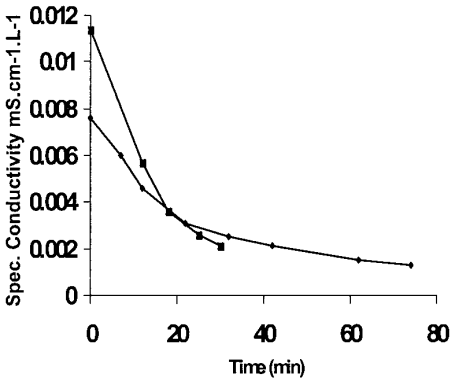

Figure 4. Conductivity measurement ($mS \cdot cm^{-1} \cdot L^{-1}$) during electrodialysis of skim milk (◆) and defatted skim milk (■).

3.2. Phosphocasein preparations

The performance of the electrodialysis unit during skim milk demineralisation was monitored by means of conductivity measurements (Fig. 4). Because of the different starting volumes of skim milk for the control and MF (defatting) treatments, milk conductivity ($mS \cdot cm^{-1}$) values were expressed per unit volume of milk, i.e. $mS \cdot cm^{-1} \cdot L^{-1}$ (Fig. 4). in order to provide a common basis for comparing the rates of conductivity decline. The objective during ED processing was to reduce the concentration of soluble milk salts (as reflected by conductivity readings) of both treatments to about the same level, i.e. stopping short of destabilising micellar casein through removal of colloidal salts. Processing times of 30 min and 74 min were recorded for 850 L of control and 500 L of MF (defatted) skim milks according as they reached their respective conductivity levels of 0.0026 and 0.0013 $mS \cdot cm^{-1} \cdot L^{-1}$.

An attempt to reduce the residual level of fat in skim milk by MF (using a 1.4 μm membrane) did not appear to succeed in reducing fat content any further judging from the measured values of 0.061% and 0.068% for microfiltered and original skim milks, respectively (Tab. I). Although, fat content in the defatted, demineralised phosphocasein powder (1.61%) was lower than the control (4.31%), it also happened that the dried phosphocasein prepared following electrodialysis only (i.e. without further defatting) had a comparably low fat content (1.76%) also (Tab. II).

The total protein content (80.29%) of the spray dried phosphocasein control produced using 140% added diafiltration water was of a similar order to that already reported by Jost and Jelen [11] and Pouliot et al. [19]. For some unexplained reason, lower protein contents of 68.28% and 61.91% were obtained in the phosphocaseins produced from the demineralised and MF defatted, demineralised skim milks, respectively even though similar diafiltration levels and process conditions were utilised throughout all trials. Non-casein nitrogen in the case of the phosphocaseins prepared after electrodialysis was higher (~ 2 ×) than that of the control (Tab. II).

The total Ca content of defatted, demineralised skim milk was reduced to 33% of its original level, while that of the soluble Ca was reduced by one-half (Tab. I). Both total and soluble phosphate removal levels were in the order of 50%.

Partial demineralisation by electrodialysis reduced the ash content of phosphocasein powders by approximately 50% to 3.72–4.33% (Tab. II). Total Ca (7.4 $mg \cdot g^{-1}$) was less than one third that of the control (26.8 $mg \cdot g^{-1}$), while soluble Ca was considerably reduced from 0.25 $mg \cdot g^{-1}$ to 0.06 $mg \cdot g^{-1}$ as a result of the diafiltration effects during MF (Tab. II). Phosphate levels were similarly affected, except for more moderate reductions (~ 50%) in total P possibly due to the contribution of organic P residues. The mean micellar size and zeta potential of control phosphocaseinate, dispersed in SMUF at pH 6.6, were 165 nm (± 1.5 nm) and –18.2 mV (± 0.5 mV), respectively. Micellar size were lower than the 240 nm quoted by Famelart et al. [2] for native phosphocaseinate dispersed in ultrafiltrate, and may have been due to protein separation from a late lactation (November) milk.

Relatively short run times (< 18 min maximum) were recorded on the MF plant when

Table I. Effect of demineralisation by electrodialysis and defatting (by microfiltration) on the composition of skim milk.

Constituent	Skim milk	Demineralised (ED) skim milk	Defatted (MF), demineralised (ED) skim milk
Total solids (%)	9.30	8.00	7.88
Total Protein (%)	3.20	na	2.73
NCN (%)	0.115	na	0.102
NPN (%)	0.029	na	0.026
Total Ca ($mg \cdot g^{-1}$)	1.20	0.40	0.40
Total P ($mg \cdot g^{-1}$)	0.90	0.50	0.50
Soluble Ca ($mg \cdot g^{-1}$)	0.40	0.20	0.20
Soluble P ($mg \cdot g^{-1}$)	0.40	0.30	0.20
Fat (%)	0.068	na	0.061

na: data not available.

Table II. Composition of phosphocasein powders prepared after defatting and partial demineralisation.

Constituent	MF skim milk (control)	Demineralised (ED) MF skim milk	Defatted *(by MF)*, demineralised (ED) MF skim milk	Jost and Jelen [11]
Moisture (%)	5.57	3.89	3.60	na
Total Protein (%)	80.29	68.28	61.91	*84.39*
NCN (%)	0.68	1.08	1.42	na
NPN (%)	0.23	0.23	0.23	na
Ash (%)	7.93	3.72	4.33	*8.00*
Total Ca ($mg \cdot g^{-1}$)	26.8	7.4	9.3	*34.0*
Total P ($mg \cdot g^{-1}$)	13.8	7.7	8.3	*6.9*
Soluble Ca ($mg \cdot g^{-1}$)	0.25	0.06	0.13	na
Soluble P ($mg \cdot g^{-1}$)	0.51	0.08	0.12	na
Fat (%)	4.31	1.76	1.61	*1.09*
Lactose (%)	1.90	na	na	na
pH (4.4 % w/w solution)	7.6	6.45	6.2	na

na: data not available.

operating at a volume reduction ratio of 4:1 (Tab. III) during each of the two diamicrofiltration steps in order to produce approximately 120 kg of phosphocasein retentate from the initial volumes of skim milk outlined earlier. Higher flux rates (149–162 $L \cdot m^{-2} \cdot h^{-1}$) were obtained during MF of the defatted, demineralised skim milk than for demineralised milk (140–147 $L \cdot m^{-2} \cdot h^{-1}$). In general, the MF plant was set up at the outset of each trial to operate at an uniform transmembrane pressure (UTMP) of 0.3 bar. Deviations from this target value occurred occasionally when consecutive runs took place without cleaning-in-place (CIP) being carried out. Inlet pressures to the membranes were increased to 4.7 bar in an effort to maintain flowrates in the short term, but may have aggravated fouling from previous runs and made it more difficult to 'balance' the pressure settings across the plant. In these circumstances, a decline in the permeate discharge pressure (Pout) from an initial value of 1.8 bar to < 1.0 bar by the end of the run caused UTMP to rise above its desired setting (0.3 bar). As a general observation, the electrodialysed skim milks showed a greater tendency towards fouling during MF as evidenced by the fall in permeate discharge pressure (Pout) (Tab. III).

3.2.1. Heat stability characteristics

The heat coagulation time/pH profile of all phosphocasein preparations resembled Type B milks which are characterised by the absence of a minimum deflection in their heat stability curves at ca. pH 6.8–6.9. Thus, heat coagulation time increases with increasing pH. A notable feature of the phosphocasein control is that HCT in the 6.5–7.05 pH range is < 1 min at 140 °C, but increases thereafter (Fig. 5). The phosphocaseins prepared from skim milks which had been either partially demineralised or defatted before partial demineralisation displayed better heat stability characteristics particularly in the 6.6–7.0 pH range where many low-acid foods are processed. Phosphocasein prepared from partially demineralised skim milk had higher HCT values over the entire pH range than the same milk which had been first defatted before partial demineralisation (Fig. 5). It appears that the additional removal of minerals afforded by

Table III. Membrane pressures and flow rates during phosphocasein preparation from of (i) electrodialysed and (ii) defatted, electrodialysed skim milks using the Tetra Pak Alcross™ M, Type 2 × 19 Special MF (0.1 μm) plant.

Time (min)	Pressure (bar)* in Loops 1 and 2, respectively				Flow Rate ($L \cdot h^{-1}$) combined for both Loops	
	P_{in} Retentate	P_{out} Retentate	P_{in} Permeate	P_{out} Permeate	Permeate	Retentate**
MF (0.1 μm) of demineralised skim milk						
500 L RO water added to 650 L demineralised skim milk						
0	na	na	na	na	na	na
9	4.70; 4.7	2.3	2.54; 3.05	0.45; 0.77	1940	789
18	4.55; 4.7	2.3	1.60; 2.82	0.00; 0.64	1860	na
410 L RO water added to above retentate						
0	4.65; 4.64	2.3	3.64; 3.65	1.54; 1.47	1960	843
9	4.65; 4.70	2.3	2.85; 3.30	0.77; 1.07	1775	858
17	Finish	na	na	na	na	na
MF (0.1 μm) of defatted, demineralised skim milk						
385 L RO water added to 500 L skim milk						
0	4.55; 4.50	2.3	3.83; 3.83	1.76; 1.80	2100	1064
11	4.55; 4.50	2.3	3.40; 3.48	1.41; 1.46	2030	912
14	4.55; 4.45	2.3	3.25; 3.42	0.96; 1.33	1980	na
315 L RO water added to above retentate						
0	4.55; 4.43	2.3	3.39; 3.56	1.31; 1.50	2155	na
10	4.55; 4.45	2.3	3.07; 3.43	0.96; 1.33	na	713

*: based on calibrated pressure gauge readings to an accuracy of 0.05 bar.
**: timed manual measurement.
na: data not available.

electrodialysis affects the heat stability/pH relationship of reconstituted phosphocasein solutions, and is beneficial in terms of readjusting shifts in HCT profiles away from the more typical pH range for milk that are caused by MF alone. It is not clear from the results so far whether MF defatting of skim milk prior to demineralisation had a negative influence on the heat stability improvements or if it were more likely due to subtle ionic changes arising from slight differences in conductivities at the point of terminating the ED processes during each treatment.

3.2.2. Rennet clotting characteristics

Rennet clotting was observed only in the control sample of MF phosphocasein suspended in SMUF or in distilled water supplemented with calcium chloride. A rennet coagulation trace of 12 min was obtained on a Formagraph, with mean K20 (rate of curd formation) and A60 (curd firmness) values of 6.88 min and 28.5 mm, respectively. The respective values for a typical milk sample are 23.5; 11.0 and 42.3. No clot formation occurred with the phosphocaseins

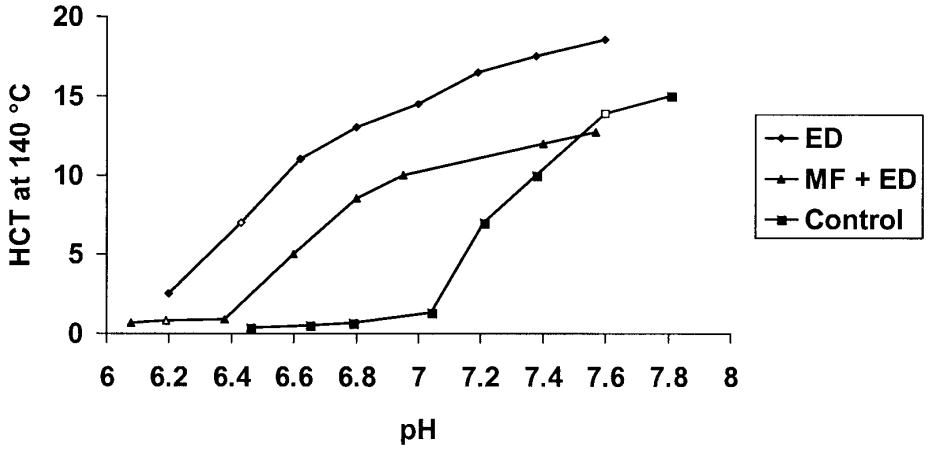

Figure 5. Effect of pH on the heat coagulation time (HCT) at 140 °C of phosphocasein solutions reconstituted to 4.4% total solids. Open symbols represent the unadjusted pH of each protein solution.

prepared from partially demineralised skim milk, irrespective of whether pro-coagulation conditions were facilitated by the presence of added Ca during reconstitution.

4. DISCUSSION

As all the membrane processes in the study were commissioned within the recent past, a certain amount of familiarisation during initial trials was required in the course of aiming to attain optimum plant settings. The UF plant proved challenging and the relatively poor performance on non-MF defatted rennet whey was probably due to start up on whey after completing an acid wash cycle. This would have contributed to a tightening of membranes, and may have been further compounded by the drop in whey pH prior to processing. A much more satisfactory performance was obtained during the subsequent trial based on MF defatted whey. Judging from all 4 UF trials, it is clear that a starting volume well in excess of 5000 L of whey is necessary so that the residual quantity of concentrated of high protein retentate exceeds the dead volume (127 L) of the plant and enables the final solids concentration to be optimised before drying.

In the case of developing defatted WPC's, further work will be undertaken to determine if an improved performance may be achieved by defatting partially concentrated UF retentate initially rather than raw whey itself. The MF defatting trials undertaken with raw whey to date were aimed at providing a benchmark setting for future work.

Detailed compositional analysis is currently being undertaken to establish an explanation for the poor gelation characteristics of all the experimentally- produced WPC's. Careful attention is being given to the ionic nature of the reconstituted proteins. Britten and Pouliot [1] obtained poorer gels with WPC's produced from cheese whey (optimum gel strength at pH 4.0) compared to those obtained from milk microfiltrate. Addition of ionic Ca (5–15 mmol·L^{-1}) increased gel strength according as pH increased in the order pH 8 > pH 6 > pH 4 [1]. Insufficient data, however, was available at the time of writing in order to make a judgement on the relative merits of UF processing at lower temperatures vis-à-vis protein functionality.

The functional properties of phosphocasein were affected by partial demineralisation (ED) prior to MF separation. A loss of rennetting properties was accompanied by some gains in heat stability. It is not clear whether electrodialysis was also responsible for the lower level (62–68%) of casein enrichment compared to the control, given similar processing conditions. A slight decline in permeation rates coincided with a drop in permeate outlet pressures and caused uniform transmembrane pressure to increase beyond desirable levels. Due to relatively short processing times, it was not possible to say whether the flux decline was due to greater fouling associated with casein destabilisation as a result of progressing demineralisation of skim milk a step too far.

4. CONCLUSION

An extensive amount of data is being built up on operating conditions likely to be used in experimental investigations that involve the integration of a number of sequential membrane processing steps in a large pilot scale facility. Preliminary studies indicate that high protein WPC's and phosphocasein products may be prepared without undue processing delay. Phosphocasein enriched powders with dedicated functional properties may be produced through control of the mineral content of milk prior to MF. However, adequate volumes of whey are required when operating in a batch concentration mode in order to overcome plant dead volume effects and ensure that a high concentration factor is achieved during the final stages of UF processing of high protein WPC's.

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