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Partitioning of calcium and magnesium (total divalent cations) during membrane filtration of milk

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ABSTRACT

Partitioning of total divalent cations (TDVC) during reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) has been investigated. During RO, there was an increase in TDVC and Ca^{2+}, and a reduction in the ethanol stability of RO retentates. During UF of milk at its normal pH, there was an increase in total divalent cations, but only a slight increase in Ca^{2+} in the retentate. There was some loss of micellar calcium during UF. However, the ratio of amounts of soluble to total divalent cations in the retentate decreased as concentration factor increased. During NF, a small amount of TDVC was found in the permeate and TDVC rejection was estimated to be about 0.83.

During UF of milk, the amount of TDVC in permeate increased significantly as the pH was reduced over the range 6.7–5.1 and the concentration of Ca^{2+} also increased both in the retentate and the permeate. However, this was not reversible, as when milk was restored to its original pH, its Ca^{2+} remained higher and ethanol stability was lower. In contrast, for whey and for UF permeate, changes in Ca^{2+} were reversible, when they were subject to similar pH changes. During UF, TDVC concentration in permeate decreased as temperature increased, due to the lower solubility of calcium phosphate at higher temperature. Ca^{2+} in permeate also decreased as UF temperature increased.

1. Introduction

The main membrane techniques for processing milk are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Factors affecting permeate rates and reducing concentration polarisation and membrane fouling have been well researched (Renner and AbD El-Salam, 1991; Field et al., 1995; Youravong et al., 2003). UF has been used for determining the amounts of calcium, magnesium and phosphorus, which are not associated with the casein micelle (Davies and White, 1960). At the normal pH of milk, approximately 30% of the calcium, 65% of the magnesium and 45% of the phosphorus is in the diffusible form. These increase as the pH is reduced, by whatever means. Glover (1985) reported that the ratio of soluble to total divalent cations (TDVC) decreased from 29% in raw milk down to 7% in milk concentrated 5-fold by UF. Changes in pH have been found to influence the amount of minerals in the final retentate during UF of whey and buttermilk (Hiddink et al., 1978). It was observed that maximum mineral removal was obtained by UF at pH 6.6, followed by diafiltration at pH 3–3.5. It has been observed that the rejection of calcium, sodium and phosphorus was higher during diafiltration than UF and that diafiltration of acidified milk gave rise to lower rejections of calcium, phosphorus and sodium (Bastian et al., 1991). Calcium and *P* recovery in UF concentrates (CF = 5) were 84% for calcium and 66% for *P*. These were reduced by diafiltration and UF of acidified milk.

Premaratne and Cousin (1991) reported the following concentration factors for some different divalent and trivalent cations resulting from a five-fold concentration of milk by UF: Zn (4.9), Fe (4.9), Cu (4.7), Ca (4.3), Mg (4.0) and Mn (3.0). This suggested that there were differences in their binding capacities to casein and whey proteins. Retentates produced by UF of skim milk were able to withstand sterilisation at 120 °C for 7 min (Sweetsur and Muir, 1985). The heat stability was improved by procedures which reduced the levels of salts in the retentates. In milk concentrated two-fold by UF, it was noted that Ca^{2+} in the retentate immediately after production was slightly lower than in the original milk, but increased slightly during storage, by up to 15%. Ca^{2+} in permeate was reported to be only one third of that in the milk (May and Smith, 1998).

Partitioning of minerals in milk when pH is reduced has been well researched (Holt et al., 1981; Holt, 2004). Both pH reduction and heating will result in movement of calcium and *P* between the micelle and the soluble phase. The reversibility of this move-

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ment and how it might influence the stability of the casein micelle has been less studied.

Ultrafiltration at high temperatures has not been studied in depth. Rose and Tessier (1959) and Pouliot et al. (1989a,b,c) used UF to look at mineral partitioning at high temperature and found that soluble calcium decreased as temperature increased. Sood and Kosikowski (1979) reported that UF at 60 °C resulted in a higher permeate rate than at 50 °C.

This paper investigates factors affecting calcium losses of TDVC from UF retentates during membrane processing, and how TDVC and Ca^{2+} in UF permeate are influenced by pH and temperature.

2. Materials and methods

Raw milk was obtained from The Centre for Dairy Research, University of Reading (CEDAR). It was centrifuged using a separator (R.A. Lister and Co., Ltd., Dursley, UK) to produce skim milk which was stored at 4 °C prior to concentration by a variety of membrane processes.

2.1. Membrane processing

2.1.1. RO and UF

Skim milk was ultrafiltered using an Aquious PCI (Hants, UK) tubular system, surface area 0.8 m^2, fitted with ES625 membranes (MWCO, 25 kDa,) at 50 °C. The inlet and outlet pressures were 6 bar and 2 bar, respectively. Samples were taken from the retentate when concentration factors reached 1.25, 1.75 and 2.65.

Skim milk was concentrated with an Aquious PCI RO tubular unit at 50 °C, fitted with AFC99 membranes. Its surface area was 2.6 m^2 and the inlet pressure was 40 bar. Samples were taken from the retentate and permeate when concentration factors reached 1.25, 1.50, 1.75, 2.00 and 2.40.

2.1.2. Combined UF and NF

Skim milk was UF treated using the PCI tubular Module, at conditions described earlier, until the solids content in the milk retentate increased by a factor of about 4. TDVC and Ca^{2+} concentrations were measured in both retentates and permeates at different concentration factors. The UF permeate was collected and nanofiltered the following day at 20 °C–5.6-fold total solids concentration in NF retentate, using PCI AFC30 NF membranes of surface area 0.8 m^2 at a pressure of 25 bar.

2.1.3. Effect of pH on calcium loss in UF-reversibility studies

Two batches of skim milk were ultrafiltered by the PCI tubular module in the constant recycle mode. In the first batch, UF commenced at 7 °C and increased to 25 °C, while in the second batch a constant temperature of 30 °C was maintained throughout. During the UF process, milk pH was reduced in stepwise fashion by adding 5 M HCl and then raised by adding 5 M NaOH back to the original milk pH level. Samples of milk retentate and permeate (25 mL) were collected for measuring TDVC and Ca^{2+} concentrations at different pH values.

After adjusting pH by adding either HCl or NaOH, permeates were collected after 5 and 10 min at each pH, as well as after 30 min for both lowest and highest pH levels. TDVC concentration in permeate and pH value in milk were measured to observe how quickly they came to equilibrium after pH adjustment.

To understand more clearly the reversibility of movement of TDVC when altering pH, the pH of milk was adjusted in stepwise fashion during UF at 30 °C to pH 5.40 with 5 M HCl and then adjusted back to its original pH with 5 M NaOH Ca^{2+} and ethanol stability were measured. For comparison with skim milk, samples of cheese whey and UF permeate were subjected to the same changes.

2.1.4. Effect of temperature on calcium loss during UF

Skim milk was ultrafiltered in the constant recycle mode using the PCI module. Temperature was changed throughout the process by means of a heat exchanger in the circuit; ranges used were 5–25 °C, 26.5–55.5 °C and 60–10 °C, over a period of about 90 min.

Approximately 25 mL samples of milk, retentate and permeate were taken at various temperatures from the system for measuring both TDVC and Ca^{2+} concentrations (at 20 °C).

2.1.5. Analytical procedures

Retentates and permeates were analysed for TDVC and Ca^{2+}. TDVC concentration was shown as the average of three measurements by the EDTA titration method. The procedure involved titrating 5 mL milk, 1 mL ammonia buffer solution (7 g ammonium chloride and 25 g ammonia solution, specific gravity 0.88, made up to 100 mL with distilled water) and 0.02 mL calmagite indicator against 0.01M EDTA solution until the colour of milk changed from pink to blue (On-Nom et al., 2010).

Ca^{2+} concentration was measured using a Ciba Corning 634 ISE Ca^{2+} analyser (Siemens Diagnostic, Newbury, UK) (Lin et al., 2006a). The electrode was calibrated using five Ca^{2+} standards on a daily basis. A Ciba Corning 250 analyser combined with a Patterson calcium direct*ION* flow cell (Patterson Scientific Ltd., Luton, UK) was used for acidified samples, as they had higher Ca^{2+} values.

Ethanol stability was determined by mixing milk samples with equal volumes of different strength ethanol solutions, at 1% intervals. The ethanol stability was recorded as the highest concentration which just failed to cause the milk to coagulate.

3. Results

3.1. Comparison of UF and RO retentates

Results are shown for how various milk properties change as milk is concentrated by RO and UF in Table 1. TDVC increased in a linear fashion with concentration factors for both UF and RO retentates (R^2 = 0.964 for UF). During RO, the Ca^{2+} concentration in milk increased by a factor of 1.31, from 1.74 mM to 2.28 mM at concentration factor 2.40. Ethanol stability decreased from 82% to 68% at a concentration factor 1.25, then at a reduced rate to 60% at a concentration factor of 2.40. In contrast, Ca^{2+} level increased by much less during UF, by a factor of 1.04, from 2.15 mM to 2.23 mM at a concentration factor 2.65. Also, as expected, increases in TDVC were lower for UF than for RO at equivalent concentration factors. The ethanol stability of UF retentate remained at 82% up to a concentration factor 1.75, decreasing slightly to 80% at a concentration factor 2.65 and appeared to be influenced more by the composition of the soluble phase than by the protein. In a second UF trial, TDVC concentration in UF retentate increased by 2.77-fold, from 34.8 mM to 96.4 mM at a concentration factor of 4 (Table 2). Loss of TDVC from the retentate was calculated to be 30.3%. During UF, TDVC in the permeate increased only slightly, from 9.0 mM to 11.6 mM. The ratio of soluble to TDVC was 12% at this concentration factor. However, Ca^{2+} concentrations in both UF retentate and permeate remained constant throughout the concentration process, with only a slight increase in milk concentrated to 3-fold and 4-fold. Also, Ca^{2+} in permeate was lower than in retentate for samples taken at different concentration factors.

Colloidal calcium and magnesium can be estimated by subtracting TDVC in permeate from that in the retentate. Colloidal TDVC in the feed was thus estimated to be 25.8 mM, whereas in the 4-fold retentate it was 84.8 mM. Thus, if no colloidal TDVC were lost, the expected concentration in the retentate would be 103.2 mM, indicating a considerable loss resulting from UF. This loss must arise