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Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation

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Abstract

This study investigates fouling of membranes during membrane distillation (MD) of two model dairy feeds - skim milk and whey, as well as their major single components. Every MD experiment was conducted for 20 hours at 54 °C feed inlet temperature and 5 °C permeate inlet temperature using PTFE membranes. Performance was assessed in terms of throughput (flux) and retention efficiency. Skim milk flux was found to be lower but stable over time compared to whey. The study using single components as well as combinations thereof revealed that fouling was primarily driven by proteins and calcium, but only in combination. Lactose also played a role to a lesser extent in the protein/membrane interactions, possibly due to preferential hydration, but did not interact with the membrane polymer directly. However lactose was found to deposit once an anchor point to the membrane was established by other components. Skim milk showed strong adhesion from its principle proteins, caseins; however salts were needed to form a thick and dense cake layer. Caseins seem to form a layer on the membrane surface that prevents other components from interacting with the membrane polymer. Whey proteins, on the other hand, deposited to a lesser extent. In

general, membrane distillation was found to be a process that generates high quality water with retention of all tested components >99% while simultaneously concentrating whey or skim milk.

Introduction

Membrane distillation (MD) is a relatively recent commercial membrane process with research on its applicability in various industries progressing rapidly. For dairy applications, MD with its theoretical 100 % retention bears the advantage to concentrate and recover high-quality water in a single process. Another potential feature is the more gentle processing of heat-sensitive ingredients compared to current evaporative technologies [1]. Key to successful MD operation is the hydrophobic membrane, which needs to remain hydrophobic in the presence of the feed components. The dairy streams that are investigated here have complex chemistries containing components (e.g. fats and proteins) which are known to foul hydrophobic membranes. Fouling is a major obstacle for efficient membrane operation for all membrane processes as it reduces flux through the membrane [2] via pore blockage and plugging. Additionally, MD membrane fouling also increases the risk of membrane wetting by compounds migrating into the membrane pores and plugging of the flow channel which may lead to a pressure increase up to the liquid entry pressure (LEP) of the membrane [3, 4].

Fouling during MD manifests itself as a decrease in flux over time due to higher thermal resistance and temperature polarization, and reduced area and increased tortuosity for mass transfer. It is a result of specific interactions between the membrane and various solutes in the feed-stream, and between the absorbed solutes and other solutes in the solution as well as compaction of the deposited layer upon interaction between components in that layer [5, 6]. Each component of a feed-stream will interact differently with the membrane. Protein conformation, zeta potential, and other factors will influence these membrane-solute interactions [7], and it is expected that the

chemistry of the dairy components will dictate the ultimate fouling mechanisms in MD processing of dairy applications.

Skim milk and whey are two major dairy streams that are often processed using membrane technologies. Average compositions of the solids in skim milk and whey are shown in Figure 1.

Figure 1: Dry-matter composition of left: skim milk and right: whey as reported by a local manufacturer and used in this study

Caseins are the major group of milk proteins and form micelles in milk which consist of sub-micelles linked together via colloidal calcium phosphate bridges [8]. Caseins are all hydrophobic in the following order from highest to lowest: β -casein > κ -casein > α_{s1} -casein > α_{s2} -casein [9]. A higher portion of κ -casein with its soluble hydrophilic glycol-peptide is located at the micelle surface forming a 'hairy' layer thus providing colloidal stability in solution [8]. Besides caseins, the remaining milk proteins are termed whey proteins, because they remain in the whey after cheese making. These proteins tend to unfold at around 60 °C, irreversibly denature above 70°C and can aggregate under certain conditions of pH, concentration and temperature [10]. The main whey proteins are α -lactalbumin (α -LA), β -lactoglobulin (β -LG) and bovine serum albumin (BSA). It is expected that all these proteins, due to their complex and dynamic surface chemistries, will interact with hydrophobic surfaces. Typical adsorbed amounts for the individual proteins at non-porous hydrophobic surfaces would be between 1-4 mg/m² [11-13]; however, when interacting with surfaces in the presence of other components this can lead to far greater fouling. When considering the porous nature of the membranes, this adsorbed amount can become even higher due to internal deposition.

Dairy fouling studies to date have primarily focused on the more common pressure driven membrane filtration processes [2, 14-18] which utilize low hydrophobicity membranes (e.g. RO membranes which typically have contact angles between 60° and 70° [19]). The present study

investigates the impact of various combinations of the different milk and whey components on MD performance. The interactions of milk components with the membrane, and the resulting fouling, are expected to be different from those of pressure driven processes since MD uses highly hydrophobic membranes (e.g. PTFE membranes which have a contact angle above 120° [20]). In addition, it uses vapour pressure as the driving force instead of mechanical pressure. The aim of the present work is to characterize the interactions of milk constituents in direct contact MD and the impact of these interactions on membrane fouling during processing.

Experimental

Direct contact membrane distillation (DCMD) system

The equipment used to test DCMD with dairy solutions is shown in Figure 2. PTFE flat-sheet membranes (Ningbo Chanqi, China) of $0.5\ \mu\text{m}$ nominal pore size and about $20\ \mu\text{m}$ thickness, with a woven (scrim) polypropylene support were used in a laboratory scale Osmonics SEPA CF module (GE Osmonics, Minneapolis, MN, USA) housing providing an effective membrane area of $0.014\ \text{m}^2$. A peristaltic pump with two heads provided a steady flow on both, feed and permeate, sides. On the permeate side cold stripping water was circulated to provide the temperature difference and to allow vapour condensation on the cold side. All four inlet and outlet temperatures were measured as well as both inlet pressures. Flux was measured by continuously and automatically recording permeate weight gain in the closed circuit.

Figure 2: Laboratory scale DCMD set-up for operation at constant concentration

For steady state experiments, an additional 'interval' timed peristaltic pump was set up to return the accumulated permeate to the feed tank every 30 mins to a fixed level and the accumulation was allowed to restart.

Operating procedure

A new membrane was used for each experiment and performance was benchmarked under standardized conditions: 54 °C feed in, 5 °C permeate in, flow of 0.047 m·s⁻¹ (200 mL/min) on both sides of the membrane. The flow rate was chosen relatively low to ensure pressure never exceeded 10 kPa to exclude any effect from an increasing pressure. Moderate increases in pressure have been shown to compress PTFE MD membranes [21] and led to reduced flux, but it was not expected to be significant in these experiments because the pressure was never observed to go beyond 10 kPa. Deionised water was used for benchmarking and flux recorded after a one hour stabilization phase. Operating conditions for experiments were kept consistent with benchmarking parameters.

Dairy fluids

As free fatty acids and phospholipids potentially lead to wetting of the hydrophobic membrane, only fat free streams were used. All dairy streams tested were based on 20 % total solids and prepared by dispersing skim milk and whey powders in deionised water. This means that the skim milk and whey solutions with all components added had a dry-matter concentration of 20 wt%, samples which only contained some components had an accordingly lower concentration to present their actual concentration in the original 20 wt% dry-matter solution as shown in Table 1.

Table 1: Dry-matter concentration of single components

Sample	Dry-matter concentration
Skim milk	
Casein	6.3 wt%
Lactose	10.2 wt%
Salts	1.8 wt%
Whey	
WPI	2.0 wt%
Lactose	15.4 wt%
Salts	2.6 wt%

To prevent microbial growth, 0.2 g·L⁻¹ of sodium azide (Sigma-Aldrich, St Louis, USA) was added to the feed solution. The skim milk and whey powders were provided by a local manufacturer, as were the 99.5% purity lactose powder and the whey protein isolate (WPI) of at least 90 % protein purity

used for the single component study. Casein was technical grade, purchased from Sigma Aldrich.

Dairy salt solutions were made according to the recipe shown in Table 2.

Table 2: Milk salt recipe according to [22]

salt	mM
Na ₃ citrate · 2H ₂ O	2.7
Citric acid · H ₂ O	7.91
K ₂ SO ₄	1.03
K ₂ HPO ₄	2.99
KH ₂ PO ₄	10.8
KOH	14.93
MgCl ₂ · 6H ₂ O	4.08
CaCl ₂ · 6H ₂ O	5.1
NaHCO ₃	10
4 N NaOH solution	Milk pH = 6.7
4 N NaOH solution	Whey pH = 6.3

Analytical methods

Retention analysis

Observed rejections of components during membrane distillation were calculated for each component by:

$$R_i = 1 - \frac{C_{P,i}}{C_{R,i}}$$

where $C_{P,i}$ and $C_{R,i}$ are the measured concentrations of component i in the permeate and retentate.

The permeate concentration was calculated from the actual concentration and the dilution factor due to the stripping water.

Wet-chemistry analyses of fouling layers

To analyse the composition of fouling layers after experiments, the membranes were cut into 14 cm² strips and soaked in 2 ml of deionised water over night at 50 °C. The membrane surface was then scraped with a surgical blade to remove all matter remaining on the membrane into the original

soaking water. The resulting solution was left at 50 °C again until all particulates were dissolved. After this removal procedure there was no visible fouling left on the membrane and no visible particles in the soaking water. The concentration of foulant compounds per cm² of membrane was calculated from the concentration in the soaking water determined by the difference in the initial and final weight.

Lactose HPLC

Lactose in the fouling layer samples was detected by a HPLC system (Shimadzu, Kyoto, Japan) as reported elsewhere [23]. For this, 900 µl samples were filtered through 0.45 µm syringe filter into HPLC sample bottles. An Agilent Zorbax Carbohydrate column and a light-scattering detector were used. The flow rate was set to 1.4 ml per minute, the mobile phase consisted of 75 % acetonitrile and 25 % HPLC grade water. Standards of 0.05, 0.1, 0.2, 0.5, 1 and 2% lactose were run to produce a calibration curve. The injection volume was 10 µl.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Permeate and retentate as well as fouling layer samples were analysed for cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, P) using a Shimadzu ICP E-9000 unit (Kyoto, Japan). Samples containing a high amount of proteins were subjected to a wet-digestion step prior to ICP-analysis as suggested by Kira et al. [24]. Aliquots of 100 µL of sample were mixed with 1 mL of HNO₃ (65 % v/v) and heated to boiling temperature for at least an hour or until de-coloration occurred leaving a clear solution as evidence of organics being fully digested. The digested sample and 10 mL of HNO₃ (5%) were transferred into a volumetric flask and filled to the standard volume using deionised water to dilute samples as needed to achieve a total solid concentration below 0.1 %. Permeate samples and samples not containing organics were acidified using the same amount of HNO₃ but were not subjected to a digestion step. Permeate samples were not diluted. All samples were filtered through a 0.45 µm syringe filter into ICP sample bottles. All calibration solutions were prepared using standard solutions for each element following a dilution scheme to establish a calibration curve for each mineral.

Total Organic Carbon (TOC) and Total Nitrogen Analysis (TN)

Samples were analysed for total organic carbon and total nitrogen using a Total Organic Carbon and Total Nitrogen Analyzer (Shimadzu V_{CSH}). Sample preparation only involved dilution to below 100ppm of carbon. Retention of total nitrogen was measured as an indicator for protein retention, here samples needed to be diluted below 50 ppm of nitrogen. Standard solutions of 100 ppm potassium hydrogen phthalate (KHP) for TOC and 50 ppm potassium nitrate (KNO₃) for TN analysis were used to confirm the original calibration. To convert the nitrogen reading to milk protein, the nitrogen measurement is multiplied by a factor of 6.38. This is equivalent to the Kjeldahl method which is officially recognised as a standard reference method in food science and technology [25].

Scanning Electron Microscopy (SEM)

The morphology of the fouling layers after MD testing was studied using a bench-top SEM (Nikon/JEOL Neo- Scope JCM-5000) applying a voltage of 10 kV and using a secondary electron detector. Samples were dried in a vacuum oven over night and 2 min gold coated (Nikon/JEOL, NeoCoater).

Reflectometry

Reflectometry is an optical measurement for component adhesion on even surfaces. The principle and method of this technique are explained in detail elsewhere [12, 13]. Strips of prime grade 150 mm silicon wafers type P/B with <1-0-0> orientation (WaferNet Inc., San Jose, CA, USA) were ethanol cleaned, dried and spin-coated (30 seconds, 2500 rpm) with an amorphous fluoropolymer (DuPont Teflon AF). To ensure full vaporisation of volatiles from the Teflon coating, the silicon strips were heated to 350 °C for at least one hour after spin-coating. The Teflon coating represents the membrane material and uniform thickness of the coatings were checked by computer controlled null ellipsometry (Sentech instruments GmbH). For the silicon substrate, a refractive index of 3.85 with imaginary part 0.02 [12] was used and the refractive index used for the PTFE top layer was 1.35. The coated silicon strips were then inserted into the measurement cell of the reflectometer. Buffer and fouling solutions entered the cell directly onto the Teflon surface via gravity feeding and were

removed by overflowing from the cell. All experiments were carried out at flow rates between 0.8 and 1.2 mL·min⁻¹. Fouling solutions need to be of low concentration for this analysis due to the laser passing through the solution. They were prepared by dissolving 1 g·l⁻¹ of the respective foulant in a phosphate buffer at pH 7 to reproduce conditions of the natural dairy streams.

A linearly polarized He/Ne laser beam entered the measurement cell through a 45° glass prism and left the cell through a second 45° prism. It is split into its parallel and perpendicular components by a polarizing beam splitter, intensities of the normal and parallel components were recorded over time. The change in intensity of the reflected polarized laser was recorded, the strength of this signal change can be converted to actual adsorbed amounts using a 5-layer matrix model [26, 27] when the refractive index increment of the adsorbing component is known. However in the current study, a mixture of various components was used and therefore we report the raw signal strength only.

Results and Discussion

Retention analysis

Retention of different minerals, organic carbon and nitrogen indicates if components pass the membrane for which they would need to penetrate into membrane pores. It was found that retention of all measured components under described experimental conditions was around 99-100 % which confirms the expected high retention of the MD process and that no milk or whey components are volatile at the low test temperatures. Especially, low-molecular weight components of non-protein-nitrogen have been found to pass through RO membranes [28] but were retained during MD.

Single component study

Flux measurements

As shown in previous work [29], skim milk and whey behave differently during MD processing. MD performance under steady state operating conditions is shown in Figure 3 and Figure 4 for skim milk, whey and various constituent combinations. After 30 minutes of processing when the first value was measured, the skim milk flux was $3 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ which is <15 % of the pure water value ($22 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). Once established, the flux remained constant over time for the skim milk experiments. For whey experiments, however, flux started close to the pure water value of $22 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and dropped continuously during the experiment to <20 % of the original value within 18 hours. The different rate of flux decline observed for skim milk and whey components suggests different fouling layer formation mechanisms and fouling layer properties.

Figure 3: Performance of skim milk components during DCMD

The component study of skim milk revealed that any stream containing caseins exhibited a low, but consistent flux over time. Caseins in combination with dairy salts led to a significant flux reduction compared to caseins in combination with lactose (or just caseins on their own).

The combination of casein and salts led to a greater flux reduction than the casein and lactose sample despite the fact that it had a lower dry-matter concentration (8.1 wt%) than the 'casein & lactose' sample (16.5 wt%). This suggests that there are interactions between caseins and salts which contribute to flux decline more than the expected flux decline associated with an increased dry-matter concentration [30]. The 'casein & NaCl' sample was adjusted to same ionic strength as the 'casein & salts' sample showing that the type of salt does have a bearing on performance and the flux reduction is not based on electrostatic interaction alone. Caseins are known for their capability to form gels at high concentrations and in the presence of bi-valent salts, they can bind 2 g of water per gram of protein [9]. These conditions are present at the membrane surface where all components are present in high concentrations, so this could explain the severe flux decline of the

'casein & salt' sample. The lower flux of the 'casein & lactose' sample (16.5 wt%) compared to just casein (6.3 wt%) could be explained by the higher dry-matter concentration. Also, the 'casein & lactose & salts' sample showed almost identical behaviour to skim milk showing a good correlation when using separate components.

Figure 4: Performance of whey components during DCMD

In contrast to skim milk, whey single components (Figure 4) always showed a continuously decreasing flux over time. Salts appeared to be involved in all the cases of great flux decline over time. The influence of lactose is also a major difference between the skim milk and the whey fouling behaviour. In the case of skim milk, lactose had little effect on flux, whereas the presence of lactose in the presence of salts had a profound effect on the fouling in the whey experiments. However, adding lactose to the whey proteins without salts being present barely affected flux despite the higher dry-matter concentration of the combined solution. The flux reduction for the lactose stream on its own is comparable to that recorded for new membranes in pure water (in the order of 13 %) and is expected to be due to compaction of the new membrane during initial use.

The data presented in Figure 3 and Figure 4 suggests that fouling is largely dependent on the presence of salt-protein interactions for skim milk and salt-mediated protein-lactose interactions for whey, and subsequently that interactions are governed by the type of protein present. The slower rate of fouling in the whey case further suggests that the protein-lactose-salt interactions are more sensitive to concentration under the test conditions.

Visualisation of the fouling layers via SEM images

SEM pictures of the membranes used during the skim milk single component study are shown in Figure 5. The typical web structure of a new PTFE membrane (top left) was completely covered by a thick and uniform fouling layer after skim milk fouling (top right). The layer formed by 'Casein & salts' (middle left) appears similar to the skim milk fouling layer. 'Casein & lactose' (middle) only formed a thin layer with the membrane web structure still being recognizable underneath. Based on flux results it was assumed that lactose did not interact with caseins, however the formation of a fouling layer in the 'casein & lactose' experiment is consistent with the work of other researchers who found that sugars enhance casein-casein interactions by reducing a partial osmotic pressure and therefore increasing electrostatic attraction and hence gel formation [31]. Caseins on their own did not form a visible layer that completely covered the membrane, which explains the relatively high flux for the casein dispersion.

Figure 5: SEM pictures of fouling layers of skim milk component study

The SEM images of the whey fouled membranes are shown in Figure 6. Similarities with the skim milk component layers shown in Figure 5 include the lactose, salts and combined lactose and salts samples (please note that the concentrations are higher for whey components). Lactose on its own did not show any sign of fouling, suggesting that flux reduction was more likely due to membrane morphology changes. Salts on the other hand formed a continuous and homogeneous crystal layer that covered the membrane. When salts were tested together with lactose, crystallisation also occurred but was patchy and heterogeneous, not covering the entire membrane area. Other studies [32-35] found that homogeneous crystallization is due to bulk precipitation in the feed that settles onto the membrane surface, forming a layer while heterogeneous crystallization is due to surface crystallization (scaling). Calcium salts can increase solubility of lactose due to complex formation between the salt and lactose [36, 37], therefore preventing crystallization in the feed bulk. However,

at the membrane surface concentrations are much higher so that crystallization can still occur leading to heterogeneous rather than homogeneous scaling.

Figure 6: SEM of fouling layers of whey component study

The whey experiment images show similar outcomes to skim milk experiments, where a thick fouling layer was only formed for the whole solution (i.e., whey or skim milk) and the protein & salts samples, but not for the whey protein solution on its own. The results for the protein alone, however, were different. A slight coating of the membrane surface was observed with the pure whey protein solution, whereas caseins on their own did not appear to form such a coating. The whey protein coverage of the membrane did not, however, adversely affect flux. The flux was greater for the whey protein alone experiment than for the casein alone experiment. The 'whey protein & lactose' fouled membrane revealed some spots on the membrane where crystals, presumably lactose, had formed but overall the membrane surface was clean.

Composition of fouling layers

Figure 7 shows compositions of the fouling layers after each of the skim milk component runs.

Figure 7: Fouling layer compositions of skim milk components

The skim milk fouling layer consisted mostly of protein. The similar composition of the 'casein & lactose & salts' sample compared to skim milk indicates that the effect of whey proteins in skim milk is minor compared to caseins as this is the main difference between these two solutions. In the case

of 'casein & lactose', less overall fouling occurred, but more lactose than protein deposited on the surface, indicating that caseins need salts to form a thick deposit layer. This is also evident in the comparison of the 'Casein & salts' results with the 'Casein' results. Comparison of the amount of protein deposited in the 'Casein & salt' result with that of the 'Casein & lactose & salts' results also confirms the conclusion from the flux data that lactose does not play a major role in skim milk protein fouling in the presence of salts. It is noteworthy, however, that as lactose on its own did neither show in the SEM nor in the scrapped deposit layer, its presence in the combined 'casein & lactose' sample confirms interaction between casein and the membrane as lactose on its own cannot interact with the membrane polymer. After protein interaction with the membrane polymer, lactose could then anchor with the casein via hydrogen bonding and deposit [38].

The 'casein & NaCl' sample with same ionic strength as the 'casein & salts' solution showed similar levels of protein as the casein sample alone, however it led to more flux decline than the casein sample which could be due to salts reducing the electrical double layer around the proteins allowing them to approach more closely [39]. However, a large amount of protein deposited only when bivalent ions were present. Calcium is a known foulant, not only due to precipitation, but also because it can influence the electrical double layer of proteins much more, allowing them to approach more closely and gel. It can also act as a bridge between the membrane and proteins, as well as between proteins, especially with phospho-proteins like caseins [7, 40]. When adding lactose to casein & salts, less protein deposited which could be attributed to preferential exclusion of lactose, resulting in a greater hydrophilicity of the protein [31]. The presence of salts in the 'casein' and 'casein & lactose' samples can be related to calcium being released from the micelles when flowing along the membrane surface as confirmed by the mineral compositions shown in Table 3. In general, it seems that phosphorus and calcium are the main minerals deposited during fouling approximately in a ratio of 2:1 calcium:phosphorus.

Table 3: Minerals in deposit layers for skim milk component samples

Sample Name	Component concentrations (all in $\mu\text{g}/\text{cm}^2$)				
	Ca	K	Mg	Na	P
Skim milk	66	3	4	8	33
Casein & lactose & salts	65	3	5	6	33
Casein & lactose	10	2	0	1	0
Casein & salts	55	3	5	3	28
Casein & NaCl	3	1	0	11	1
Salts & lactose	160	28	1	31	93
Casein	4	1	0	0	0
Salts	24	2	2	0	11
Lactose	0	1	0	0	0

The compositions of whey component fouling layers are shown in

Figure 8. Some similar observations can be made between the whey and skim milk fouling layer analyses. In both cases the 'salts & lactose' fouling layers show very high lactose deposition in tandem with the minerals. The precipitation taking place in the 'salt & lactose' experiment is difficult to explain, but may possibly involve the formation of calcium–lactose complexes [41] at the air–water interface which is hydroxide ion rich due to negative adsorption, or binding of lactose to calcium ions [37]. Such crystallization did not occur when proteins were present which could be explained by salt/protein interactions reducing nucleation for crystal growth. The buffering capacity of milk proteins against salt precipitation is well known [42, 43]. In the case of caseins it is due to two thirds of total calcium occurring in colloidal form and being associated with casein micelles [44]. Also, whey proteins are able to bind calcium when the pH exceeds the iso-electric point of the proteins and they carry a negative charge [45].

The similarity of the whey data to the skim milk data with respect to the effect of lactose in the presence of salt is, however, surprising. The flux data (Figure 4) showed that lactose has a profound effect on fouling in the presence of whey protein and salts, but the amount of protein present in the fouling layer (Figure 8) shows that the amount of protein deposited is not affected by the presence

of lactose in the presence of salt. This suggests that the effect of lactose is not (only) on the quantity of protein deposited but on the structure or permeability of the protein fouling layer.

Figure 8: Fouling layer composition of whey component study

Whey proteins on their own were only found in very low concentration in the fouling layer. Once salts were introduced, protein fouling became substantial. Also, for the 'salts & lactose' sample, a very high amount of lactose was found on the membrane surface but still this sample led to equivalent flux as the 'WPI & salts' solution which revealed much less material depositing on the membrane surface. This could be due to whey components blocking the pores by entering them instead of forming a thick surface layer that reduces mass transfer.

In general, mineral content of fouling layers was much higher in this work than found in UF fouling by Begoin et al [46], who reported 0.4 % of dairy fouling to be of mineral origin. However, UF membranes allow salts to permeate while salts are retained during MD. Salts can precipitate on the membrane because of poor solubility or due to charge interaction with the membrane. Their interactions with proteins also increase protein deposition. The single mineral analysis (Table 4) revealed that the same as for skim milk fouling, mostly calcium and phosphorus, the ions that have most charge and influence the double layer of proteins to the largest extent, deposited when salts were on their own or in combination with lactose.

Table 4: Minerals of scraped deposit layers for whey component samples

Sample Name	Component concentrations [all in $\mu\text{g}/\text{cm}^2$]				
	Ca	K	Mg	Na	P
Whey	55	4	3	7	7
WPI & lactose & salts	61	7	2	4	12
WPI & lactose	4	2	0	1	0
WPI & salts	32	10	2	7	10
Salts & lactose	200	50	0	43	120
WPI	3	1	0	0	0
Salts	100	14	7	16	55
Lactose	2	1	0	0	0

Interactions between membrane polymer and feed components

Reflectometry measurements allow *in-situ* observations of component adhesion that is due to interactions between foulants and a membrane-resembling surface. Such measurement excludes flux and concentration polarisation effects for convenient exploration of just the interaction chemistry.

Figure 9 shows the deposition speed and final adsorbed amount (signal strength) of skim milk components. Caseins together with calcium phosphate (the main salt that deposited during flux tests) resulted in fastest adsorption, while addition of lactose to the protein/salt mixture reduced the adsorption rate and the adsorbed amount, again confirming that lactose influences the adsorption behaviour of casein. Casein & lactose had a faster adsorption rate than only caseins. This again shows that lactose requires other components to be able to deposit onto the membrane surface.

Figure 9: Adsorbed amount and adsorption rate of skim milk components on a PTFE coating. CN = casein, CaP = calcium phosphate

Adsorption rate and adsorbed amount of whey components is illustrated in Figure 10. Both, Figure 9 and Figure 10 confirm that lactose on its own cannot adsorb onto the PTFE surface and calcium

phosphate only deposited in very low amounts. However, considering the low mass of Ca, this low adsorbed amount required substantial interaction with the polymer surface. For the salts & lactose samples, membrane performance differed from reflectometry results. This again supports the proposition that high local concentrations present at the membrane surface due to permeate removal lead to supersaturation of salts and lactose and that polymer foulant interactions were not the critical mechanism for fouling.

Figure 10: Adsorption amount and reaction time of whey components on a PTFE coating. WPI = whey protein isolate, CaP = calcium phosphate

Whey resulted in faster adsorption rates and higher adsorbed amounts than those of the combined whey proteins alone. Whey proteins appear to be able to adhere to the PTFE surface, but require salts to establish a fouling layer through association between proteins and salts. This is in line with membrane flux decline presented in Figure 4 where flux was not greatly reduced in the presence of whey proteins alone. 'WPI & CaP' had the fastest adsorption of all samples, however in combination with lactose it resulted in a higher overall mass adsorbed but occurred at a slower rate. Also, WPI combined with lactose resulted in slightly slower but higher values compared to WPI alone, which is also in agreement with membrane flux performance. Again, this indicates that lactose interacts with other components and increases adsorbed amounts by increasing the total deposited mass once it has interacted with other feed components.

Comparison of Figure 9 and Figure 10 reveals approximately the same initial adsorption rate and adsorption amount for whey and skim milk. The results for 'WP & lactose' and 'CN & lactose' are also similar. The effect of addition of calcium phosphate to the protein, however, results in much greater and faster adsorption in the case of whey than in the case of skim milk. This is contrary to the flux data that showed that the addition of salts containing calcium phosphate resulted in more fouling in the case of skim milk than in the case of whey. This suggests that the whey protein fouling layer in

the presence of salts contains a greater quantity of foulant, but the fouling layer formed is less resistant to flux, possibly by having a more open and permeable structure.

Addition of lactose in the presence of protein and calcium phosphate further increases the quantity adsorbed in the whey case, but decreases the quantity adsorbed in the skim milk case, with the rate of initial adsorption decreasing in both cases. This seems to correlate well with the slow but severe fouling observed in the whey protein in the presence of lactose and salts case, but does not correlate with the fast and severe fouling in the case of casein in the presence of lactose and salts.

Possible fouling mechanisms

A possible mechanism behind these fouling observations for skim milk is given in Figure 11. It is proposed that, for skim milk, fouling is dominated by the interaction of the milk proteins (caseins) and calcium ions. The soluble casein micelles deform due to applied shear stresses resulting in exposure of hydrophobic regions, which in turn interact with the hydrophobic membrane forming a thin layer on the membrane fibres with the hydrophilic regions facing the bulk feed stream. In addition, the evaporation of water near the membrane surface is similar in nature to the operation of e.g. a spray drier, leading to concentration and/or precipitation of less soluble caseins possibly also induced by local high ionic concentrations. Caseins have a higher water binding capacity than whey proteins and can therefore form dense gels [38]. Intact and hydrophilic micelles passing within the bulk stream adhered to these 'membrane - attached' micelles, but only form a layer due to charge on the micelles and salts. In the case where salts are not present, the micelles passing by did not attach to the layer formed on the membrane due to the same charge of the micelles resulting in repulsion between the micelles. Therefore, no gel layer was formed and in turn flux was higher (Figure 3).

Figure 11: Possible fouling mechanism of PTFE membrane by caseins and salts during DCMD

Whey fouling was much less pronounced than that of skim milk and also much less whey protein deposited compared to caseins. However, total flux reduction at the end of each run was similar. A possible mechanism behind the whey fouling behaviour is that whey proteins aggregate over time depending on concentration, temperature and shear rate [47-49].

It is proposed that, for whey, fouling is dominated by whey protein–lactose–calcium interactions. The role of each of the three components in this interaction is not clear. In contrast to the fouling involving casein, whey protein fouling from whey seems to involve lactose. Although the effect of lactose on proteins is not well understood yet [38], it is known that lactose can interact directly with proteins by disrupting or changing their hydrogen bonding networks [38]. Sugar addition leads to diminished water activity which makes water-protein interactions less effective and lactose can interact with proteins directly via hydrogen bonds [38]. The amount of lactose interaction with the whey protein component was found to also depend on the presence of salts. In the absence of salts, lactose addition to whey protein did not influence flux or measured adsorption, and SEM pictures only revealed localised crystals on an overall clean membrane surface. In the presence of salts, however, the reverse is the case. Lactose addition to whey protein led to much more fouling. Lactose was also found to be able to interact with the membrane and with salts in the absence of protein. A fouling layer containing calcium and lactose was formed at the membrane surface in the absence of whey protein (i.e. for the “Lactose & salt” solution). It is believed that calcium can interact with lactose to form calcium-lactose complexes [41]. A fouling mechanism can, therefore, be envisaged where calcium and lactose form a calcium – lactose soluble complex at the air/water interface or at the hydrophobic membrane/water interface, and the passage of protein in this calcium and lactose rich region results in the interactions of these components with the whey protein, changing the 3D protein structure to such a degree that it is no longer soluble and forms a fouling layer. This is, however, a speculative proposal that can only be supported by more research.

Conclusions

MD was found to be a feasible process to concentrate skim milk and whey that simultaneously allows production of high purity water. Major findings include the observations that retention was independent of component composition and always above 99%, and membrane wetting was not observed in any case even after prolonged runtimes of around 20 hours. The single component studies revealed a complex set of interactions between the protein component, lactose and salts, and that this interaction is governed by the protein type present. It was found that fouling developed faster when salts were present in solution. Caseins seemed to form a more extensive layer on the membrane than whey proteins, and this is expected to be due to hydrophobic interactions with the polymer which are stronger than for whey proteins. Lactose cannot interact with the membrane on its own, however it does interact with other components through hydrogen bonds or charge interaction and can deposit once an anchor point to the membrane is established by other components. It was shown that MD can be carried out under realistic runtimes for commercial application in the dairy industry for skim milk and whey-like streams as experiments were carried out for runtimes of around 20 hours which is the maximum runtime in an industry where daily cleaning is necessary to prevent microbial growth. Despite the analysis of flux and fouling layers of a matrix of solutions representing skim milk and whey, a better understanding of the interaction chemistry would compliment these findings and will improve the process further.

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References

1. Christensen, K., R. Andresen, I. Tandskov, B. Norddahl, and J.H. du Preez, Using direct contact membrane distillation for whey protein concentration. *Desalination*, 2006. 200(1-3): p. 523-525.
2. James, B.J., Y. Jing, and X. Dong Chen, Membrane fouling during filtration of milk--a microstructural study. *Journal of Food Engineering*, 2003. 60(4): p. 431-437.
3. El-Bourawi, M.S., Z. Ding, R. Ma, and M. Khayet, A framework for better understanding membrane distillation separation process. *Journal of Membrane Science*, 2006. 285(1-2): p. 4-29.
4. Gryta, M., Fouling in direct contact membrane distillation process. *Journal of Membrane Science*, 2008. 325(1): p. 383-394.
5. Bottino, A., G. Capannelli, O. Monticelli, and P. Piaggio, Poly(vinylidene fluoride) with improved functionalization for membrane production. *Journal of Membrane Science*, 2000. 166(1): p. 23-29.
6. Tolkach, A. and U. Kulozik, Transport of whey proteins through 0.1 mm ceramic membrane: phenomena, modelling and consequences for concentration or diafiltration processes. *Desalination*, 2006. 199(1-3): p. 340-341.
7. Cheryan, M., in *Ultrafiltration and Microfiltration Handbook*. 1998, Technomic Pub: Lancaster.
8. De Kruif, C.G. and C. Holt, *Casein micelle structure functions and interactions*, in *Advanced Dairy Chemistry-Proteins Part A*, P.F. Fox. and P.L.H. Mcsweeney, Editors. 2003, Kluwer Academic, Plenum Publishers: New York. NY p. 233 - 270.
9. Fox, P.F., *Developments in Dairy Chemistry-4: Functional Milk Proteins* 1990: Elsevier Applied Science.
10. Sing, H. and P. Havea, *Thermal denaturation, aggregation and gelation of whey proteins*, in *Advanced Dairy Chemistry-Proteins Part A*, P.F. Fox. and P.L.H. Mcsweeney, Editors. 2003, Kluwer Academic, Plenum Publishers: New York. NY p. 1263 - 1281.
11. Waninge, R., P. Walstra, J. Bastiaans, H. Nieuwenhuijse, T. Nylander, M. Paulsson, and B. Bergenstahl, Competitive Adsorption between β^2 -Casein or β^2 -Lactoglobulin and Model Milk Membrane Lipids at Oil/Water Interfaces. *Journal of Agricultural and Food Chemistry*, 2005. 53(3): p. 716-724.
12. Nady, N., K. Schroën, M.C.R. Franssen, R. Fokkink, M.S. Mohy Eldin, H. Zuilhof, and R.M. Boom, Enzyme-catalyzed modification of PES surfaces: Reduction in adsorption of BSA, dextrin and tannin. *Journal of Colloid and Interface Science*. 378(1): p. 191-200.
13. Schroen, C.G.P.H., A. Roosjen, K. Tang, W. Norde, and R.M. Boom, In situ quantification of membrane foulant accumulation by reflectometry. *Journal of Membrane Science*. 362(12): p. 453-459.

14. Piry, A., W. Kühnl, T. Grein, A. Tolkach, S. Ripperger, and U. Kulozik, Length dependency of flux and protein permeation in crossflow microfiltration of skimmed milk. *Journal of Membrane Science*, 2008. 325(2): p. 887-894.
15. Mourouzidis-Mourouzis, S.A. and A.J. Karabelas, Whey protein fouling of microfiltration ceramic membranes--Pressure effects. *Journal of Membrane Science*, 2006. 282(1-2): p. 124-132.
16. Grandison, A.S., W. Youravong, and M.J. Lewis, Hydrodynamic factors affecting flux and fouling during ultrafiltration of skimmed milk. *Le Lait*, 2000. 80: p. 165 - 174.
17. Bouzid, H., M. Rabiller-Baudry, L. Paugam, F. Rousseau, Z. Derriche, and N.E. Bettahar, Impact of zeta potential and size of caseins as precursors of fouling deposit on limiting and critical fluxes in spiral ultrafiltration of modified skim milks. *Journal of Membrane Science*, 2008. 314(1-2): p. 67-75.
18. Jimenez-Lopez, A.J.E., N. Leconte, F. Garnier-Lambrouin, A. Bouchoux, F. Rousseau, and G. Gésan-Guiziou, Ionic strength dependence of skimmed milk microfiltration: Relations between filtration performance, deposit layer characteristics and colloidal properties of casein micelles. *Journal of Membrane Science*, 2011. 369(1-2): p. 404-413.
19. Akin, O. and F. Temelli, Probing the hydrophobicity of commercial reverse osmosis membranes produced by interfacial polymerization using contact angle, XPS, FTIR, FE-SEM and AFM. *Desalination*. 278(13): p. 387-396.
20. Hwang, H.J., K. He, S. Gray, J. Zhang, and I.S. Moon, Direct contact membrane distillation (DCMD): Experimental study on the commercial PTFE membrane and modeling. *Journal of Membrane Science*. 371(12): p. 90-98.
21. Zhang, J., J.-D. Li, and S. Gray, Effect of applied pressure on performance of PTFE membrane in DCMD. *Journal of Membrane Science*, 2011. 369(12): p. 514-525.
22. Santos, A., M. Ladero, and F. García-Ochoa, Kinetic Modeling of Lactose Hydrolysis by a [β]-Galactosidase from *Kluyveromyces Fragilis*. *Enzyme and Microbial Technology*, 1998. 22(7): p. 558-567.
23. Ramchandran, L., P. Sanciolo, T. Vasiljevic, M. Broome, I. Powell, and M. Duke, Improving cell yield and lactic acid production of *Lactococcus lactis* ssp. *cremoris* by a novel submerged membrane fermentation process. *Journal of Membrane Science*. 403-404(0): p. 179-187.
24. Kira, C.S. and V.A. Maihara, Determination of major and minor elements in dairy products through inductively coupled plasma optical emission spectrometry after wet partial digestion and neutron activation analysis. *Food Chemistry*, 2007. 100(1): p. 390-395.
25. Metsämuuronen, S., M. Mänttari, and M. Nyström, Comparison of analysis methods for protein concentration and its use in UF fractionation of whey. *Desalination*. In Press, Corrected Proof.
26. Dijt, J.C., M.A.C. Stuart, J.E. Hofman, and G.J. Fler, Kinetics of polymer adsorption in stagnation point flow. *Colloids and Surfaces*, 1990. 51(0): p. 141-158.

27. Dijt, J.C., M.A.C. Stuart, and G.J. Fler, Reflectometry as a tool for adsorption studies. *Advances in Colloid and Interface Science*, 1994. 50(0): p. 79-101.
28. Yorgun, M.S., I.A. Balcioglu, and O. Saygin, Performance comparison of ultrafiltration, nanofiltration and reverse osmosis on whey treatment. *Desalination*, 2008. 229(13): p. 204-216.
29. Hausmann, A., P. Sanciolo, T. Vasiljevic, E. Ponnampalam, N. Quispe-Chavez, M. Weeks, and M. Duke, Direct Contact Membrane Distillation of Dairy Process Streams. *Membranes*, 2011. 1(1): p. 48-58.
30. Martinez-Diez, L. and M.I. Vazquez-Gonzalez, Temperature and concentration polarization in membrane distillation of aqueous salt solutions. *Journal of Membrane Science*, 1999. 156(2): p. 265-273.
31. Dickinson, E. and L. Matia Merino, Effect of sugars on the rheological properties of acid caseinate-stabilized emulsion gels. *Food Hydrocolloids*, 2002. 16(4): p. 321-331.
32. Boerlage, S.F.E., M.D. Kennedy, G.J. Witkamp, J.P.v.d. Hoek, and J.C. Schippers, BaSO₄ solubility prediction in reverse osmosis membrane systems. *Journal of Membrane Science*, 1999. 159(1-2): p. 47-59.
33. Dydo, P., M. Turek, and J. Ciba, Scaling analysis of nanofiltration systems fed with saturated calcium sulfate solutions in the presence of carbonate ions. *Desalination*, 2003. 159(3): p. 245-251.
34. Lee, S., J. Kim, and C.-H. Lee, Analysis of CaSO₄ scale formation mechanism in various nanofiltration modules. *Journal of Membrane Science*, 1999. 163(1): p. 63-74.
35. Lee, S. and C.-H. Lee, Effect of operating conditions on CaSO₄ scale formation mechanism in nanofiltration for water softening. *Water Research*, 2000. 34(15): p. 3854-3866.
36. J.G., Z., ed. *Whey and lactose processing*. 1992, Elsevier Science Publishers: New York.
37. Alexander, M., L.F. Rojas-Ochoa, M. Leser, and P. Schurtenberger, Structure, Dynamics, and Optical Properties of Concentrated Milk Suspensions: An Analogy to Hard-Sphere Liquids. *Journal of Colloid and Interface Science*, 2002. 253(1): p. 35-46.
38. Marti, I., P. Fischer, and E.J. Windhab. *Effect of lactose on rheology of milk protein dispersions*. in *3rd International Symposium on Food Rheology and Structure*. 2003. Zürich, Switzerland.
39. Walstra, P., T.J. Geurts, and A. Noomen, *Dairy Technology : Principles of Milk Properties and Processes*. 1999, New York: Marcel Dekker Inc.
40. Ramachandra Rao, H.G., Mechanisms of flux decline during ultrafiltration of dairy products and influence of pH on flux rates of whey and buttermilk. *Desalination*, 2002. 144: p. 319-324.

41. Commins, D.B.M., R.A.B. Hard, and T.A. Nickerson, Recovery of lactose from aqueous solutions: Precipitation with calcium hydroxide and sodium hydroxide. *Journal of Food Science*, 1980. 45(2): p. 362-366.
42. Marshall, A. and G. Daufin, Physico-Chemical aspects of membrane fouling by dairy fluids. *International Dairy Federation [Special Issue] S.I.*, 1995. 9504(Fouling and cleaning in pressure driven membrane processes): p. 8-35.
43. Salaün, F., B. Mietton, and F. Gaucheron, Buffering capacity of dairy products. *International Dairy Journal*, 2005. 15: p. 95-109.
44. Fox, P.F. and P.L.H. McSweeney, *Dairy Chemistry and Biochemistry*. 1998, London: Blackie Academic & Professional.
45. Patocka, G. and P. Jelen, Calcium Association With Isolated Whey Proteins. *Canadian Institute of Food Science and Technology Journal*, 1991. 24(5): p. 218-223.
46. Bégoïn, L., M. Rabiller-Baudry, B. Chaufer, C. Faille, P. Blanpain-Avet, T. Bénézech, and T. Doneva, Methodology of analysis of a spiral-wound module. Application to PES membrane for ultrafiltration of skimmed milk. *Desalination*, 2006. 192(1-3): p. 40-53.
47. Moro, A., C. Gatti, and N. Delorenzi, Hydrophobicity of Whey Protein Concentrates Measured by Fluorescence Quenching and Its Relation with Surface Functional Properties. *Journal of Agricultural and Food Chemistry*, 2001. 49(10): p. 4784-4789.
48. Kazmierski, M. and M. Corredig, Characterization of soluble aggregates from whey protein isolate. *Food Hydrocolloids*, 2003. 17(5): p. 685-692.
49. Karleskind, D., I. Laye, F.-I. Mei, and C.V. Morr, Gelation Properties of Lipid-Reduced, and Calcium-Reduced Whey Protein Concentrates. *Journal of Food Science*, 1995. 60(4): p. 731-737.

Highlights

- Membrane distillation (MD) was tested on whey and skim milk solutions
- No wetting and >99% rejection of all measured dairy components was observed
- Fouling of dairy components mostly involved proteins and calcium
- Protein fouling by caseins in skim milk was strongest, leading to rapid flux decline
- Lactose did not bind to the membrane, but was involved in the fouling layer