ORIGINAL ARTICLE

The effects of physicochemical changes on critical flux of skimmed milk ultrafiltration

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Abstract

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The effects of physical and physicochemical changes by modifying pH, increasing ionic strength and adding $CaCl_2$ or citrate of skimmed milk on the critical flux and fouling reversibility during ultrafiltration were studied. The critical flux of skimmed milk was decreased as skimmed milk was modified by these methods. In general, decreases in critical flux were explained well by the surface charge of the particles such as whey proteins, casein micelles, and particle size distribution. The critical flux appeared to decrease as the surface charge of these proteins decreased. The results also indicated that small particles e.g. whey proteins and casein molecules played a major role in determination of critical flux. The fouling reversibility appeared to be dependent on physicochemical properties of skimmed milk. Fouling reversibility decreased (irreversible fouling increased) when lowering the pH, increasing ionic strength and adding $CaCl_2$ and increased when increasing pH and adding citrate.

Key words : critical flux, ultrafiltration, particle size, fouling

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In ultrafiltration (UF) of skimmed milk, the physicochemical properties of the feed have a major impact on membrane fouling. A fouling layer, composed of protein and mineral complexes forms on the membrane surface. The properties of this fouling layer largely control the membrane performance. Preventing or reducing the formation of this fouling layer by using the critical flux concept or making this layer more reversible, could enhance the performance of the membrane processes. The reversibility of fouling layer as well as the critical flux of colloid and protein suspensions appear to be dependent on hydrodynamic conditions and physicochemical properties (Bacchin *et al.* 1996, Chen, 1998, Huisman *et al.* 1998 and Kwon and Vigneswaran, 1998). In UF of skimmed milk, changes in ionic strength, pH and ionic calcium may affect the critical flux and the properties of this fouling layer. The effect of pH and ionic calcium on the permeate flux and cleaning efficiency of skimmed milk has been studied by several researchers (Patel and Rueter, 1985, Vetier, *et al.* 1988 and Attia *et al.* 1991, Eckner and Zottola, 1993). However, no information of these effects on fouling reversibility has been reported. Critical fluxes of various feed materials have been studied by Field *et al.* 1995, Chen, 1998 and Wu *et al.* 1999. Youravong *et al* (2002) determined the critical flux of milk protein suspensions. They found that critical flux of milk protein suspensions, sodium caseinate and whey protein depended on the hydrodynamics and their physicochemical properties. However, for a complex system as skimmed milk, no information of critical flux has been reported.

The purpose of this study was to investigate the effect of changing pH, ionic strength, adding calcium (which increases both particle size and ionic calcium concentration) and citrate (which decreases particle size and ionic calcium concentration) of skimmed milk UF on (i) critical flux and (ii) fouling reversibility. This information may lead to more understanding of the fouling mechanism and suggest optimized conditions for skimmed milk UF regarding the fouling problem.

Material and Methods

Preparation of modified skimmed

Pasteurised skimmed milk was kept at 4 ^{o}C and used within 3 days to reduce any changes in physicochemical properties. Physicochemical properties of skimmed milk were modified by adjusting pH, increasing ionic strength (adding NaCl), adding $CaCl_2$ and citrate ($Na_3C_6H_5O_7.H_2O$). The final protein concentration after any adjustment was controlled at 3.1 %. Modifications were performed at 50 ^{o}C with gradual addition of the solutions and gentle mixing. The modified skimmed milk was held at 50 ^{o}C for 30 min before introduction to the membrane rig.

Modified pH

The pH of skimmed milk was modified by slowly adding NaOH (0.2 M) or HCl (0.2 M). The range of pH (at 50 ^{o}C) studied were 5.5, 6.2, 6.6 (unmodified skimmed milk), 7.2 and 7.7.

Modified ionic strength

The ionic strength of skimmed milk was modified by adding NaCl solution. The ionic strengths studied were 0.08 M (unmodified skimmed milk), 0.18 M, 0.28 M and 0.48 M.

Adding $CaCl_2$

Adding $CaCl_2$ solution decreased the pH of skimmed milk and increased ionic calcium and the particle size of casein micelles. Thus two main conditions were studied, adding $CaCl_2$ without pH control and with pH control (6.6). Two levels of $CaCl_2$ were used (0.01 and 0.027 M).

Adding citrate

Citrate solution was added to the skimmed milk at 0.02 and 0.04 M. Adding citrate causes an increase in pH and a decrease in ionic calcium and the particle size of casein micelles. The studies were performed without pH control and with pH control (6.6).

Physical and chemical analysis

Particle size measurement

The particle size of unmodified and modified skimmed milk were determined using a particle size analyzer (Mastersizer 2000, Malvern, UK). Note that the range of particle size which can be determined using this equipment is 0.02 to 1000 µm, which is within the range of casein micelles and protein aggregates.

Zeta-potential measurement

Zeta-potential of unmodified and modified skimmed milk were determined using a zeta potential analyzer (Zetasizer 5000, Malvern, UK).

Ionic calcium

The ionic calcium of skimmed milk was determined using Ca^{2+} electrode.

Protein content

The protein content of skimmed milk (before modification) was determined using Dairylab2 (Multispec Ltd, York, UK).

Determination of critical flux and fouling reversibility index (RI)

The experiment was performed in total recycle mode at constant crossflow velocity 3.4 $m.s^{-1}$ at 50 ^{o}C. The membrane used was PVDF (FP200, MWCO 200 kDa). A cycle involving increasing and decreasing transmembrane pressure (TMP) was performed to determine the critical flux and fouling reversibility index (*RI*). The TMP was increased stepwise through 5 levels between 0.0 bar to 1.10 bar with a holding time at each TMP of 15 min (e.g. 0.05, 0.10 (TMP1 range), 0.15, 0.20, 0.25 and 1.10 (TMP2 range) bar. After that TMP was increased to pressure 3.05 bar with a holding time of 45 min. Then the TMP was decreased to TMP2 range for 15 min and to TMP1 range for at least 15 min or until a steady flux was achieved (Figure 1). Note that the permeate flux at (TMP1) both during increasing and decreasing steps was always below the critical flux.

The critical flux was estimated according to Wu *et al.* (1999). Fouling reversibility index (*RI*) was used to indicate the reversibility of fouling developed when the permeate flux went above the critical flux. *RI* is the ratio of total resistance at TMP1 (increasing step) to the total resistance at (TMP1) (decreasing step). *RI* is expressed as:-

$$RI = \frac{R_{tot(in)}}{R_{tot(in)}} \qquad (1)$$

where $R_{tot(in)}$ and $R_{tot(de)}$ are the total resistance at TMP1 when TMP was increased and decreased stepwise respectively.

If $RI = 1$, it indicates that no irreversible fouling (completely reversible) was formed when the permeate flux was above the critical flux. If $RI < 1$, it indicates the irreversible fouling formed when the permeate flux was above the critical flux.

Results and Discussion

Modifying pH and ionic strength (addition of NaCl) and adding both $CaCl_2$ and citrate caused major changes in physical and physicochemical properties. In this study the change of particle size and its distribution (casein micelle), and zeta potential were investigated. These changes were used to explain the results of the critical flux and fouling reversibility (*RI*).

Particle size, zeta potential and ionic calcium

Particle size and its distribution, zeta potential and concentration of ionic calcium of skimmed milk are presented in Table 1. The particle size here was in the range 0.07 to 0.210 µm. Alternatively, the particle size distribution could be presented using the value d(0.1), d(0.5) and d(0.9). The value d(0.1) indicates that 10 % (vol.) particles in the sample are smaller or equal to this value. The value d(0.5) indicates that 50 % (vol.) particles are smaller or equal to this value (the average of particle size). The value d(0.9) indicates that 90 % (vol.) particles are smaller or

Table 1. The absorbance, particle size and zeta potential of unmodified and modified skimmed milk

Skimmed milk	Absorbance (375 nm)	particle size (μm)			Zeta potential (mV)	Ionic Calcium (mM)
		d(0.1)	d(0.5)	d(0.9)		
Unmodified skimmed milk (pH 6.6)	2.88	0.074	0.122	0.210	-17.0(0.3)*	2.29
Adjusted pH** skimmed milk						
5.5	2.89	0.082	0.143	7.752	-12.1(0.3)	>5
6.2	2.89	0.078	0.125	0.257	-16.1(0.3)	>5
7.2	2.78	0.075	0.125	0.239	-19.1(0.2)	1.29
7.7	2.55	0.065	0.128	0.293	-20.1(1.0)	0.85
Adjusted ionic strength with NaCl						
+0.1 molar	2.88	0.075	0.123	0.212	-15.2(1.2)	3.43
+0.2 molar	2.88	0.075	0.123	0.212	-14.3(0.9)	4.28
+0.4 molar	2.87	0.071	0.121	0.209	-12.9(1.0)	>5
Added $CaCl_2$						
+0.01 molar (pH6.0)	2.87	0.084	2.073	18.91	-12.2(1.3)	>5
+0.027 molar (pH 5.5)	2.86	8.678	24.60	63.39	-10.8(0.8)	>5
+0.01 molar (pH6.6)	2.88	0.065	0.127	0.294	-15.5(1.3)	>5
+0.027 molar (pH6.6)	2.86	0.063	0.124	0.268	-15.6(3.2)	>5
Added Citrate						
+0.02 molar (pH 6.9)	2.55	0.08	0.466	4.54	-15.5(1.3)	1.14
+0.04 molar (pH7.1)	2.02	0.075	0.214	4.34	-15.6(3.2)	0.47
+0.02 molar (pH6.6)	2.76	0.067	0.139	0.99	-15.7(1.4)	1.71
+0.04 molar (pH 6.6)	2.37	0.085	0.542	5.00	-15.3(2.5)	0.72

***(Value are mean ± SD for n = 3) ; **pH at 50 °C**

equal to this value.

It is important to note that the particle size analyzer could not detect any changes of particle size below 0.02 μm. In some conditions where the casein micelle dissociates (i.e. the concentration of particles below 0.02 μm increases), the particle size changes in this region were indicated by using absorbance measurement as discussed below.

For unmodified skimmed milk, casein micelles are the major particles (Walstra and Jenness, 1984). Their particle size distribution is shown in Table 1. It can be seen the particle size was in the range 0.07 to 0.21 μm and the absorbance at 375 nm was 2.88.

When the pH was increased or citrate was added, skimmed milk became clearer and the absorbance at 375 nm decreased remarkably (e.g. 2.02 at 0.04 M-citrate). This reduction suggested that the concentration of large particles (casein micelle) decreased. The casein micelle dissociated and become individual molecules (Walstra and Jenness, 1984). Because such casein molecules are smaller than 0.02 μm, therefore they cannot be detected by this particle size analyzer. To perform a measurement, normally about 5-6 ml of (unmodified) skimmed milk was added into 100 ml of the dispersion phase (permeate) to reach the minimum light intensity, which the equipment required. The amount of milk sample required increased as pH increased or as the citrate concentration increased. For example about 30-40 ml of milk sample per 100 ml dispersion was required for skimmed milk, with 0.04 M added citrate, again indicating a decrease in the number of lager particles. Thus although the particle size distribution obtained was in the normal range for casein micelle and fat globules, the concentration of large particles have been reduced, as indicated by the drop in absorbance value of the sample directly taken from modified and unmodified skimmed milk. Le Barre and Daufin (1998) suggested that at this condition, casein micelle concentration in skimmed milk is negligible (absorbance = 2.02). The absorbance results also suggested that adding citrate with pH control resulted in an increase in concentration of large particles compared to that without pH control.

When lowering pH, or adding $CaCl_2$ the particle size increased, which can be observed by the particle size analyzer (Table 1). Although the absorbance did not change (~2.88), skimmed milk became chalkier when pH was lowered or when the concentration of $CaCl_2$ was increased. Increasing ionic strength (by adding NaCl) did not change the particle size and its distribution.

Critical flux

A cycle involving an increase and decrease of TMP during UF of skimmed milk was performed to determine the critical flux and *RI*. In some cases, the limiting flux was also obtained.

The effect of pH

A typical cycle of increasing and decreasing TMP during UF of skimmed milk (pH 6.6) is shown in Figure 1. The TMP was increased stepwise and held for 15 min. At TMP <0.23 bar, the permeate flux increased linearly with TMP. As can be seen, the TMP and permeate flux relationship started to deviate from linear when the permeate flux was above 52 kg.m^{-2}h^{-1} (TMP = 0.23 bar), giving critical flux of about 52 kg.m^{-2}h^{-1}. Increasing TMP from 0.64 to 1.05 bar very slightly increased the permeate flux (61.5 to 62.5 kg.m^{2}h^{-1}).

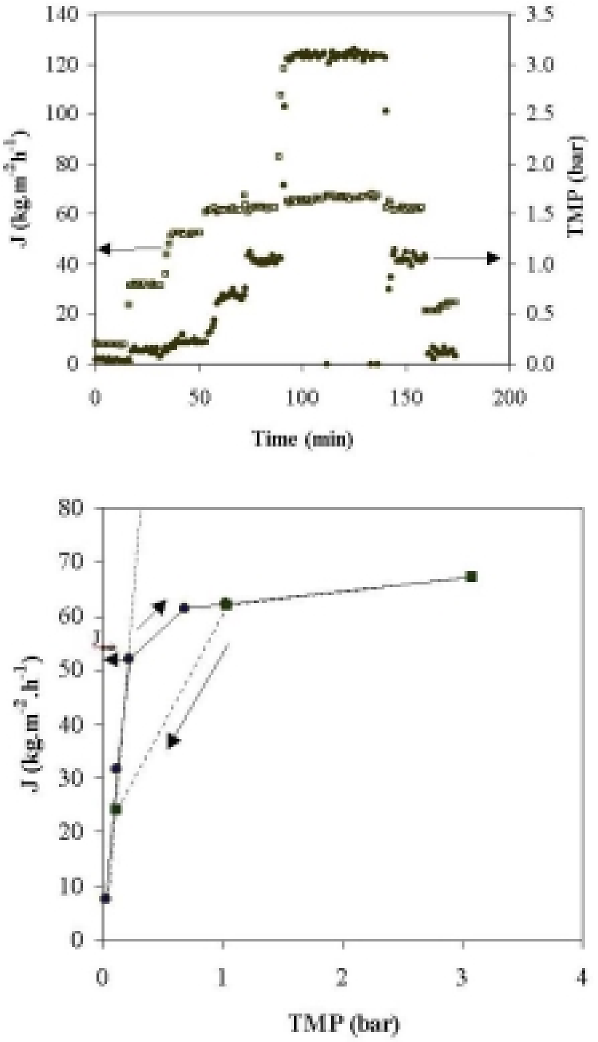

Figure 1. Permeate flux as a function of processing time and TMP during UF of skimmed milk (pH = 6.6), at crossflow velocity 3.4 m.s^{-1}, 50^{o}C.

Increasing TMP to 3.05 bar increased the permeate flux to 65 kg.m^{2}h^{-1} at the start of this TMP period level. It is interesting that at this TMP, the permeate flux increased slightly with processing time. After 45 min of processing, it was 67 kg.m^{2}h^{-1}. According to these results, the limiting flux was approximately 63 kg.m^{2}h^{-1}. When the TMP was decreased to 1.10 bar, the permeate flux was similar to that at the same TMP during the increasing period. This might suggest that no fouling had developed at TMP 3.05 bar. However, when TMP was decreased to 0.12 (TMP1) bar, the permeate flux (24 kg.m^{-2}h^{-1}) was lower than that (31.7 kg.m^{-2}h^{-1}) at 0.12 bar found in the increasing step. Note that at TMP 0.12 bar (increasing step) gave a permeate flux lower than the critical flux. This result suggested that severe irreversible fouling developed when processing was performed above the critical flux.

Similar procedures were also performed for other pH values to investigate the critical flux. The effect of pH on critical flux is presented in Figure 2. It can be seen that both increasing pH and lowering pH resulted in a statistically significant decrease in the critical flux ($P<0.05$). The critical flux at pH 6.6 (unmodified skimmed milk) was 51.5 kg.m^{-2}h^{-1}. Lowering pH to 6.2 and 5.5, decreased the critical flux to 43.8 and 38.3 kg.m^{-2}h^{-1} respectively. Increasing pH to 7.2 and 7.7 also caused a decrease in the critical flux to 46.5 and 35.5 kg.m^{-2}h^{-1} respectively.

Lowering pH of skimmed milk (pH 6.2 and 5.5), resulted in a slight increase in particle size of casein micelles (Table 1). An increase in particle size (casein micelle and protein aggregates) led to an increase in back transportation, (Davis and Leighton, 1987 and Huisman, 1998). However, this effect did not explain why the critical flux decreased because an increase in back transport should enhance the critical flux (Gesan *et al.* 1998). One possible explanation is that only the large particles (e.g.casein micelles) were involved in an increase in back transportation while small particles (e.g. whey protein) still remained on the membrane surface. The results also indicate that the large particles e.g. casein micelle did not play an important role in determination of critical flux or the onset of fouling for skimmed milk. Instead, small particles e.g. whey protein are more important in determination of the critical flux. Accordingly, this result could explain why whey protein (small particle) is the major component of skimmed milk involved with membrane fouling, which has been found by several authors for skimmed milk (Merin and Cheryan 1980, Tong *et al.* 1980 and Le Berre and Daufin, 1996). A decrease in the critical flux when pH was decreased suggests that the surface charge plays a role in determination of critical flux. Decreasing pH caused an increase in zeta potential (Table1). It was also expected that lowering pH would also decrease the surface charge of particles in skimmed milk such as, whey protein and casein micelles. A decrease in surface charge led to a reduction in repulsive electrostatic forces both between these proteins and between protein and the membrane surface. Consequently, proteins tend to deposit more on the membrane surface (Bacchin *et al.* 1995), resulting in a decrease in critical flux. This result is in agreement with the results for whey protein concentrate and sodium caseinate suspensions (Youravong *et al.* 2002) and for BSA solution (Chen, 1998).

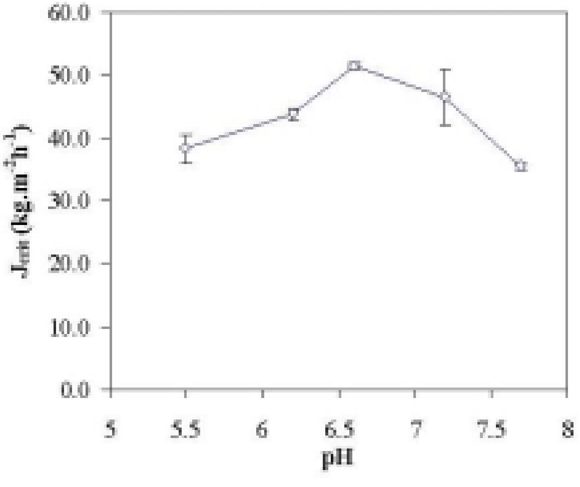

Figure 2. Effect of changing pH on critical flux during UF of skimmed milk at cross-flow velocity 3.4 m.s^{-1}, 50 °C. Error bars represent the standard deviation of three replicates

When pH of skimmed milk was increased by adding NaOH solution, the zeta potential of particles decreased. It was also expected that the surface charge of particles such as whey and casein molecule would be increased (more negative charge). As a result the electrostatic repulsion between protein and membrane would be expected to increase, resulting in enhancing the critical flux (Bacchin *et al.* 1995). However, contradictory results were observed for both protein solutions and skimmed milk. Chen (1998) found that increasing pH of BSA solution from 7.5 to 9 did not change the critical flux. Similarly, the critical flux for whey protein concentrate and sodium caseinate suspensions slightly increased when pH was increased from 7.0 to 8.0 (Youravong *et al.* 2002).

For skimmed milk, increasing pH not only increased the protein charge but also changed the particle size distribution. When the pH of skimmed milk was increased from to 7.2 and 7.7, the concentration of casein micelles in skimmed milk appeared to decrease (as indicated by a decrease in absorbance, Table 1) because casein micelles dissociated (Walstra and Jennes, 1984). As a result, the concentration of casein molecules increased (size ~15 nm), leading to an increase in concentration of small particles. These small particles therefore played a major role in the back transportation mechanism from the membrane surface. Because of their small size, the rate of back transportation or particle removal decreased (Huisman, 1998 and Davis and Leighton, 1987) and because their concentration increased, consequently, their convective transport (due to the permeate flux) would have to be reduced to balance the reduced particle removal and particle deposition (preventing accumulation), resulting in a decrease in the critical flux (Gesan *et al.* 1999).

Effect of ionic strength

The effects of ionic strength (by adding NaCl) on critical fluxes for skimmed milk is presented in Figure 3. Note that the ionic strength of unmodified skimmed milk is taken to be 0.08 M. Increasing ionic strength to 0.18 M led to a slight increase in critical flux but it was not significant compared to that for 0.08 M (P<0.05). Further increase in ionic strength, caused a slight decrease in the critical flux but it was not significant compared to that at ionic strength 0.08 M (P<0.05).

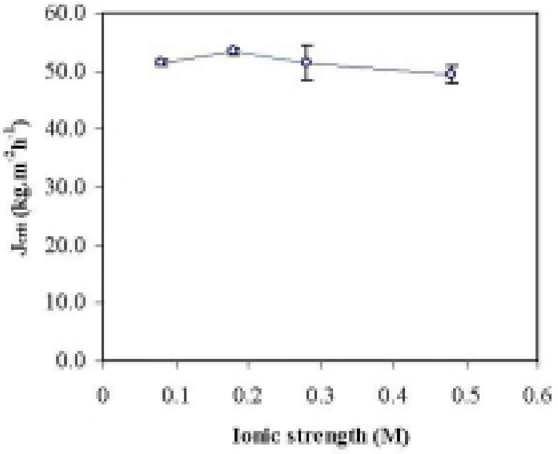

Figure 3. Effect of ionic strength (adding NaCl) on critical flux during UF of skimmed milk at crossflow velocity 3.4 m.s^{-1}, 50 ^{o}C. Error bars represent the standard deviation of three replicates

The influence of ionic strength (adding NaCl) on the critical flux of skimmed milk was similar to that found for whey protein concentrate suspension (Youravong, *et al.* 2002). However, it was not in agreement with results for sodium caseinate suspension. An increase in ionic strength caused a significant increase in zeta potential of particles in skimmed milk while the particle size and its distribution did not change (Table 1). The results from previous section of this study suggested that small particles e.g. whey protein and casein molecules played an important role in determination of the critical flux. Increasing ionic strength by adding NaCl probably not only decreased the electrostatic interaction forces (decrease the stability of protein) but also enhanced hydration of protein (Fennema, 1996). As a result increasing ionic strength may not have a significant effect on the critical flux.

Effect of $CaCl_2$

The results of critical flux is shown in Figure 4. The addition of $CaCl_2$ resulted in a significant decrease in the critical flux for both with and without pH control (P<0.05). The addition of $CaCl_2$ resulted in a decrease in pH and increased

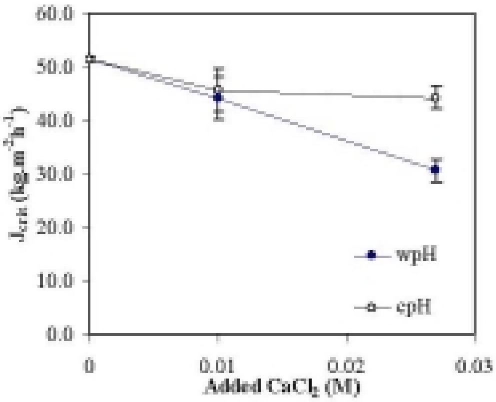

Figure 4. Effect of addition of $CaCl_2$ on critical flux during UF of skimmed milk at crossflow velocity 3.4 m.s^{-1}, 50 °C. Error bars represent the standard deviation of three replicates; wpH (without pH control); cpH (with pH control).

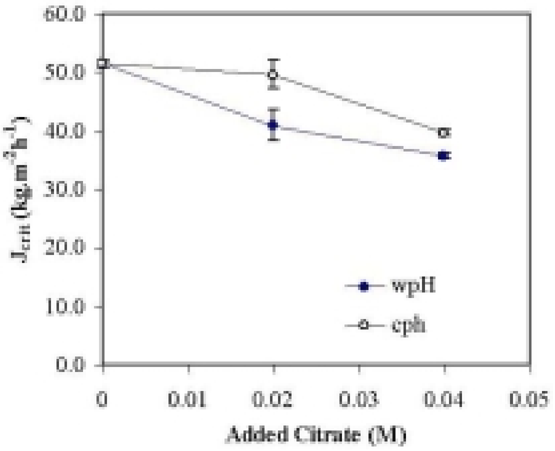

Figure 5. Effect of addition of citrate on critical flux during UF of skimmed milk at crossflow velocity 3.4 m.s^{-1}, 50 °C. Error bars represent the standard deviation of three replicates; wpH (without pH control); cpH (with pH control).

the zeta potential and ionic calcium of skimmed milk significantly. It is important to note that when $CaCl_2$ was added and the pH of skimmed milk was maintained at 6.6, the zeta potential of skimmed milk slightly decreased. A decrease in zeta potential when pH was maintained at 6.6 could be due to an increase in ionic strength (McDonogh *et al.* 1992). The particle size for controlled pH skimmed milk was slightly increased while for uncontrolled pH skimmed milk, the particle size was increased remarkably (Table 1). However, protein conformation possibly changed for both cases especially when pH was readjusted. The critical flux for both conditions was decreased compared to unmodified skimmed milk. However when the pH was controlled at 6.6, the critical flux was slightly higher than that with out controlling it. Again, it was very interesting that although the particle size increased (adding $CaCl_2$ without pH control), leading to an increase in back transportation (possibly only for large particles), the critical flux did not increase as expected. This result indicated that small particles e.g. whey protein were responsible for the determining the critical flux. A decrease in the critical flux of skimmed milk could be due to the effect of physicochemical properties of small particles e.g. surface charge rather than large particles.

Effect of citrate

The effects of addition of citrate on the critical is shown in Figure 5. Addition of citrate (both with pH control and without pH control) resulted in a significant decrease in critical flux ($P<0.05$). The addition of citrate caused a major change in particle size distribution of skimmed milk and ionic calcium. The concentration of small particles increased greatly as citrate concentration increased (Table 1). Therefore, a decrease in critical flux when citrate was added also confirmed the role small particles in determination of critical flux as discussed earlier.

When adding citrate and controlling pH, the critical flux was slightly improved compared to those without pH control but it was still lower than that of unmodified milk. This may be due to a decrease in concentration of small particle (casein molecules), resulting from an increase in concentration of large particle (casein micelles), indicated by the absorbance value) (Table 1)

Fouling reversibility

Reversibility fouling and/or amount of fouling, formed when the permeate flux was above the critical flux was indicated by *RI.*

Effect of pH

The influence of pH on *RI* is presented in Table 2. *RI* of skimmed at pH 6.6 was 0.71. Lowering the pH of skimmed milk to 6.2 and 5.5 resulted in a significant decrease in *RI* compared to that for unmodified skimmed milk (P<0.05). In contrast, increasing pH to 7.2 resulted in a significant increase in *RI* (0.80). Interestingly, when the pH was increased further (7.7) *RI* was not increased but further decreased to 0.63.

A significant decrease in *RI* when pH of skimmed milk was decreased suggested that electrostatic interaction and ionic calcium were involved in determination of fouling reversibility. When pH was decreased, the surface charge of particles such as whey proteins and casein micelles decreased, resulting in a decrease in electrostatic repulsive forces (Bacchin *et al.* 1995). This result possibly led to a decrease in fouling reversibility as suggested by Suki *et al.* (1984). Decreasing pH of skimmed milk also increased the ionic calcium (Table 1). An increase in concentration of ionic calcium possibly was also responsible for these results. It has been suggested that ionic calcium possibly acts as cement between protein molecules, casein micelles and the membrane surface and between protein, micelles themselves (Nakanishi and Kessler 1985. Vetier *et al.* 1988 and Bowen and Gan, 1990). Interestingly, when the pH of skimmed was increased, *RI* did not always increase. At pH 7.2, *RI* increased significantly. This result indicated that the fouling layer formed was much more reversible or loosely bound compared to that of unmodified skimmed milk. This result was in agreement with the results obtained by Chen, (1998) and Huisman *et al.* (1998). When the pH of skimmed milk is increased, it causes a decrease in surface charge (more negative) of milk protein. As a result, electrostatic repulsion increased. In addition, ionic calcium concentration was also decreased as pH increased, therefore it may cause an increase in fouling reversibility as discussed earlier. Under the shear (crossflow), these protein layers possibly aggregated, forming larger particles (Kim *et al.* 1992), which was more easily removed from the membrane surface. It was important to note that unlike at pH 7.2, *RI* at pH 7.7 significantly decreased compared to that of unmodified skimmed milk. This result was unexpected.

Table 2. Fouling reversibility (RI)of unmodified and modified skimmed milk during ultrafiltration

Skimmed milk	RI
Unmodified skimmed milk (pH 6.6)	0.71±0.05
Adjusted pH** skimmed milk	
5.5	0.62±0.01
6.2	0.62±0.03
7.2	0.80±0.04
7.7	0.63±0.07
Adjusted ionic strength with NaCl	
+0.1 molar	0.51±0.05
+0.2 molar	0.50±0.05
+0.4 molar	0.54±0.02
Added $CaCl_2$	
+0.01 molar (pH6.0)	0.54±0.04
+0.027 molar(pH 5.5)	0.53±0.05
+0.01 molar (pH6.6)	0.57±0.05
+0.027 molar (pH6.6)	0.35±0.05
Added citrate	
+0.02 molar (pH 6.9)	0.85±0.04
+0.04 molar (pH7.1)	0.87±0.03
+0.02 molar (pH6.6)	0.86±0.01
+0.04 molar (pH 6.6)	0.84±0.05

***(Value are mean ± SD for n = 3)**

Effect of ionic strength

The increase in ionic strength in the range 0.18-0.48 M resulted in a significant decrease in *RI* compared to that for unmodified skimmed milk (P<0.05). These results suggested that a tighter fouling layer formed under these conditions. This possibly could be due to a decrease in electrostatic repulsion force. As a result, fouling layer had a lower porosity which decreased the fouling reversibility (Le Berre and Daufin, 1998, and Mockel *et al.* 1999). In addition, increasing ionic strength also led to an increase in ionic calcium (Table 1), this may cause a decrease in the reversibility of fouling, as suggested by Vetier *et al.* (1988), Attia *et al.* (1991) and Nakanishi and Kessler (1985).

Effect of $CaCl_2$,

RI for the addition of $CaCl_2$ to skimmed milk both with and without pH control decreased significantly compared to that for unmodified skimmed milk ($P<0.05$). Without pH control, *RI* at $CaCl_2$ 0.01 M was 0.54. Further increase in concentration (0.027 M-$CaCl_2$) did not decrease *RI*. In contrast, for pH control, *RI* at 0.01 M-$CaCl_2$ was 0.57 and it decreased greatly to 0.35 at 0.027 M-$CaCl_2$.

Adding $CaCl_2$ caused an increase in zeta potential and concentration of ionic calcium. A similar result was found when the pH was decreased as mentioned earlier. The result from this study confirmed that zeta potential and ionic calcium are involved in fouling reversibility, which has been already discussed earlier.

The effect of citrate

The addition of citrate, both with and without pH control resulted in significant increase in *RI* ($P<0.05$). These results suggest that a loose fouling layer formed during these conditions. Addition of citrate led to a decrease in ionic calcium concentration which is also observed when the pH was increased. An increase in fouling reversibility therefore should be due to a decrease in ionic calcium concentration.

Conclusions

Modifying pH, increasing ionic strength and adding $CaCl_2$ or citrate caused major changes in the physical and physicochemical properties of skimmed milk, which affected the critical flux and fouling reversibility. The results indicated that small particles, e.g. whey protein and casein molecules played, a major role in determination of critical flux while larger particles, e.g. casein micelle, may not be strongly involved. The critical fluxes decrease as these small particles concentration increases. The critical flux appeared to be decreased as the surface charge of these proteins decreased (lowering pH either by adding HCl or $CaCl_2$ solution. The fouling reversibility appeared to be dependent on ionic calcium and zeta potential. In general, fouling reversibility decreased (irreversible fouling increased) when lowering the pH, increasing ionic strength and adding $CaCl_2$ and increased when increasing pH and adding citrate.

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