Chapter 4

RESULTS AND DISCUSSION

4.1 Physical and chemical characterization of commercial feed material

Physical and chemical characterizations of selected parameters (see section 3.5) were conducted to investigate the extent to which these parameters affect the ultrafiltration performance of NR latex. These parameters were particle size, zeta potential, pH and viscosity. The results were also used to determine variations in values for various feed materials ranging from fresh NR latex, to preserved latex in the form of LATZ latex and high Ammonia Latex concentrate: Modified NR Latex such as ENR 25, 50 and 60. ENR latex is structurally modified latex of an original cis-polyisoprene latex structure (Figure 4.1) which has an oxygen atom incorporated into its structure.

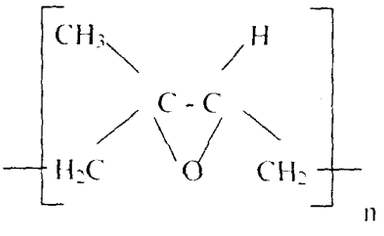

Figure 4.1- Structure of ENR Latex

The presence of oxygen [O] in the ENR makes it resistant to oil, chemical and environmental degradation (ozone, heat and water) resulting in its improvement

when it is made into products such as rubber hose or car components. ENR 20, 50 and 60 denotes the percentage of epoxidization from the original NR structure (Figure 2.1) to epoxidized structure (Figure 4.1).

The laboratory scale experiment also helps in the selection of:

(i) Suitable membrane with respect to MWCO for the ultrafiltration runs from particle size measurements.

(ii) pH requirement in preparing preservation systems: PS1 and PS2

This study also gives an idea of the physical changes that would take place such as in

(i) Viscosity changes during the concentration process by ultrafiltration from field latex to latex concentrate.

(ii) Latex stability with respect to its zeta potential values.

4.1.1 Results of chemical and physical characterization of commercial feed material

The results of this set of experiments are summarized below in Table 4.1.

4.1.1.1 Particle size

The size of the particles in fresh natural rubber latex varies over wide limits, the range 20- 5000 nm being not uncommon. Results have been reported by Van den Tempel [26] for the distributions, obtained from electron micrographs of particles hardened by bromination, of particles sizes in unconcentrated natural rubber latex.

Pendle and Swinyard [27] have presented information concerning the distribution of particle sizes in the two types of ammonia-preserved natural rubber latex concentrate, high-ammonia and LATZ low-ammonia lattices respectively. An interesting feature of the distributions, obtained by these workers is that most of them

are clearly bimodal. Typical distributions show that high-ammonia ranges are between 200-500 nm for the lower peak, and 1000-2000 nm for the higher peak. For LATZ low-ammonia the peak diameters vary somewhat, the ranges being 200-300 nm for the lower peak, and 700-1500 nm for the higher peak for the two type lattices respectively.

Analysis of Variance indicated that this apparent difference in average particle diameter between high-and low-ammonia concentrates is real, and not a consequence of random fluctuations. No comment is offered as to possible causes: there is no obvious reason why concentrates produced by the same concentration process but preserved with different levels of ammonia should tend to have significantly different average particle diameters. It may be that the difference is associated with the presence of the secondary preservatives in the LATZ lattices, but, if so, it might be expected that the average particle sizes would be larger in the low-ammonia lattices, rather than smaller, because of slight colloidal destabilization by the secondary preservatives [3].

From Figure 4.2 which shows the variation of particle size against different latex, it can be seen that the particles size for HA field latex (DRC 30%) was 0.854 μm and for LA field latex (DRC 30%) was 0.885 μm. Both these results were some what agreeable to the fact that low ammonia preservation tends to have a larger particle size compared to higher level of ammonia preservation. The presence of secondary preservatives in the case of LATZ concentrate at 60% DRC have caused colloidal destabilization by the secondary preservatives (TMTD and ZnO) as the particles size value was only 0.898 μm, smaller than compared to that of HA latex concentrate of 60% DRC which has value of 0.908 μm .

Table 4.1 Summary of results of pH, particles size, zeta- potentials and viscosity for different type of latex raw material

No.	Sample type	pH	Particle size with sonication (μm)	Particle size without sonication (μm)	Zeta potential (mV)	Viscosity (cP)
1.	AZ55 Styrene latex Standard	-	-	-	-60.9	-
2.	Distilled water	7	-	-	-20.8	-
3.	Fresh field Latex (3 hrs after tapping) (DRC 31%)	6.67	0.866	0.861	-32.9	12.0
4.	Low Ammonia field Latex (DRC30%)	9.10	0.885	0. 881	-36.9	13.0
5.	High Ammonia field Latex (DRC30%)	10.75	0.854	0.851	-55.7	17.5
6.	High Ammonia Latex Concentrate (DRC60%)	11.06	0.928	0.944	-60.1	70
7.	LA TZ Latex Concentrate (DRC60%)	9.20	0.898	0.908	-37.1	60.5
8.	ENR 25 after UF (DRC 55%)	7.70	0.919	0.925	-47.8	47.5
9.	ENR 50 before UF (DRC 26%)	8.07	0.858	1.17	-47.8	12.5
10.	ENR 50 after UF (DRC 59%)	8.76	0.876	0.876	-51.5	63.5
11.	ENR 60 before UF (DRC 26%)	7.62	0.908	0.961	-45.0	15.0
12.	Nitile Rubber Latex 48/4D	8.84	-	-	-50.2	-

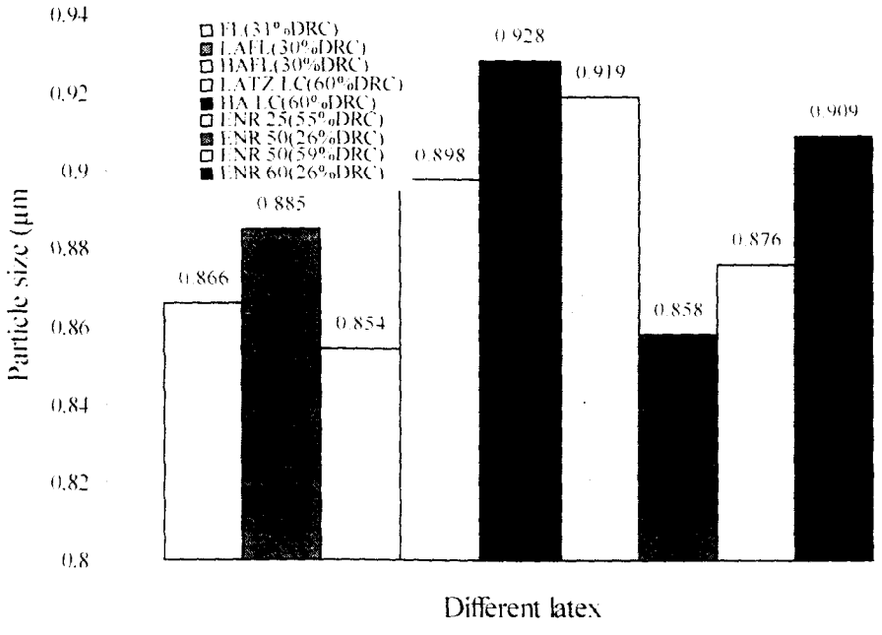

Figure 4.2 Variations of particle size with different lattices

In the case of concentrated latex, the average minimum distance between neighbouring particles is smaller. Sterically-stabilized lattices have hypothetical enlarged particles. They have a radius of $a + \lambda$, where a is the actual particle radius and λ is the thickness of the surface-bound macromolecular stabilized layer [2]. From the particle size analysis (Table 4.1) it shows that the concentrated latex such as LATZ LC and HALC, have their particle sizes increased from 0.885 µm to 0.898 µm and 0.854 µm to 0.928 µm respectively. In the case of LATZ LC the hypothetical enlargement of the particles were smaller because of the presence of a secondary preservative which caused some colloidal destabilization [2, 3].

4.1.1.2 Zeta potential

The negatively charged latex particles and its positively charged atmosphere in the presence of ammonium ions (NH_4^+) produce an electrical potential across the diffuse layer. This is highest at the surface and drops off progressively with distance, approaching zero at the outside of the diffuse layer. The potential curve is useful because it indicates the strength of the repulsive force between colloids and the distance at which the forces come to play. This is the zeta potential value of latex samples.

Zeta potential values of latex samples analyzed decreases with an increase in pH, which means that the particles will stay apart at high pH. In general the higher the value of zeta potential the more stable the particle dispersion is likely to be. The dividing line between an aqueous particle dispersion being stable and not being stable is considered to be +30mV or –30mV. So if the entire particle has a zeta potential which is more negative than –30mV or more positive than +30mV the dispersion should remain stable.

For fresh latex, the microbial activity produce organic acid that destabilize by discharging negative charges surrounding latex particles the zeta potential soon tend to drop below the stable range of +30mV or –30mV. The highly alkaline condition not only acts as a bactericide but also increases the zeta potential value. From Figure 4.3, it can be seen that highly stabilized latex have high –ve or + ve zeta potential values indicating strong repulsive action within the particles. Zeta potential is an effective tool for coagulation control because changes in zeta potential indicate changes in repulsive forces between colloids measuring stability status of the lattices [28, 29].

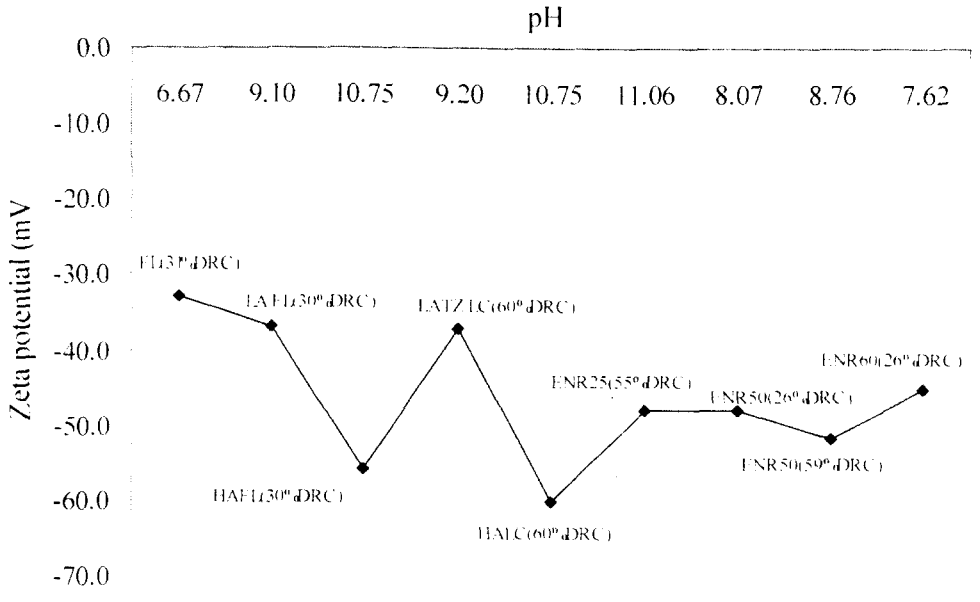

Figure 4.3 Variations of Zeta potential with pH

4.1.1.3 Viscosity

From literature [1, 2, 3, 7] the viscosity of NR latex is dependent on the following factors:

i. Average size of the polymer particles

ii. Distribution of sizes of the polymer particles

iii. Shape of the polymer particles

iv. Extent to which the particles are associated with each other

v. Viscosity of the dispersion medium.

The above factors influence viscosity. Average particle size of latex increases during preservation before concentration thus particle size distribution also vary as small particle gets into larger particle causing viscosity to increase[3].

During concentration process, dewatering removes the serum from latex causing DRC to increase as more serum is removed. Serum is the dispersing media for the latex particles. As more and more of the serum are removed, the remaining serum could be proteins of high molecular mass which are more viscous. Thus viscosity increases.

The factors mentioned above coupled with the close proximity of large particles of rubber in the absence of serum increases the viscosity value during concentration. From Table 4.1, it can be seen that the viscosity value of LA field latex after undergoing concentration to LATZ latex concentrate when the DRC value increased from 30% to 60% increases from 13.0 cP to 60.5cP. Similar trends were also observed between HA FL of 30% DRC to HA LC 60% of DRC during which the viscosity value increased from 17.5 cP to 70.0 cP.

In Figure 4.4, the plot of viscosity against DRC of various latex samples shows generally that viscosity increases with concentration (increase in DRC). Therefore, during UF experimental runs to concentrate field latex, the increase in viscosity would be a major factor to be dealt with, so due consideration would be given while carrying out this process.

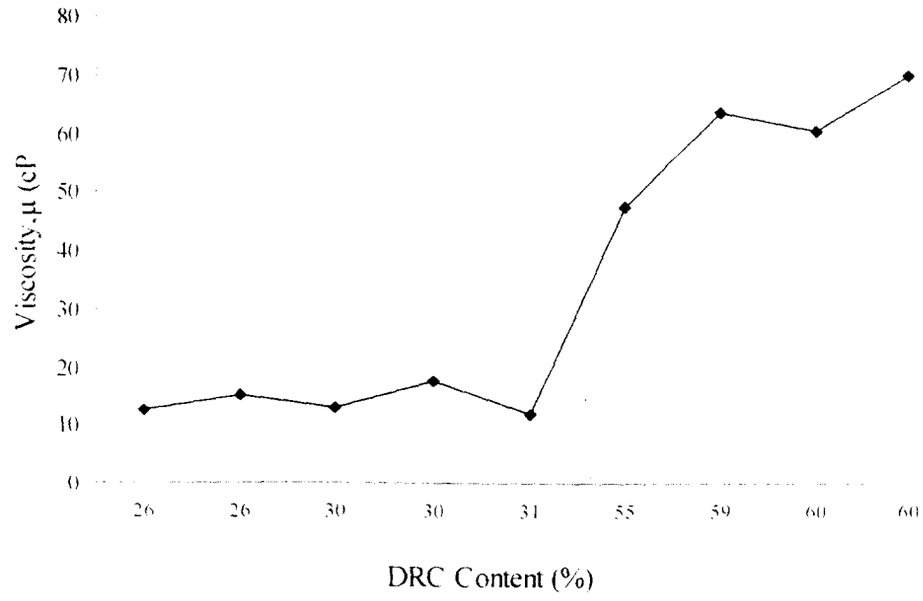

Figure 4.4 Variations of viscosity with increase in concentration (DRC)

4.2 Protein analysis

Proteins make up about 1 % to 1.5% weight of field latex (Table 2.1, Chapter 2). As the NRL is not a homogenous fluid, latex proteins are not homogenously dispersed. About 70% of latex proteins are soluble, with the remaining being associated with negatively charged membrane covering the latex particles [2, 3]. From the studies conducted by RRIM [30] molecular weight distribution of protein found in NRL vary from 5kD to 50kD. Latex protein allergy has become a major setback in the use of natural rubber latex examination glove. It is anticipated likewise, for the UF protein content can have detrimental impact as its presence affects the latex stability and contributes towards membrane fouling. Thus a good

preservation system would certainly help to arrest the bacterial degradation of protein and carbohydrate into volatile fatty acid. From investigations by Devaraj. V.. [31] it has been established that the malodor. which originates from the degraded NR latex. is caused by the presence of volatile fatty acids such as acetic. propionic. butyric. and iso-butyric and valeric acids as the products of the breakdown of carbohydrate and protein by the microbial (bacteria) degradation of NRL.

An analysis of total protein content of permeates would give an indication of the degree of preservation action of the two preservation systems tested namely. PS 1 and PS 2. This is discussed further in section 4.5 on the evaluation of suitable preservation system.

4.3 Scanning electron microscope (SEM) analysis

4.3.1 SEM micrograph of PS1 preserved latex

Figure 4.5 shows the SEM analysis of the PS1 preserved latex. which would be. used for UF Experiments. From the SEM photo. which was 7500 times. magnified show that latex particles exist as clusters of small particles. which were fairly spherical. oval and pear shaped which were formed from smaller primary particles. Schoon and Phoa [2] also reported the existence of latex particles in composite structure as shown in Figure 4.5. The average size of an individual particle as indicated in the SEM photo was about 1 μm. which would easily be rejected by 100kD MWCO FP110 PVDF membrane. 1 μm is equivalent to a MWCO of $2x10^6$ kD [32].

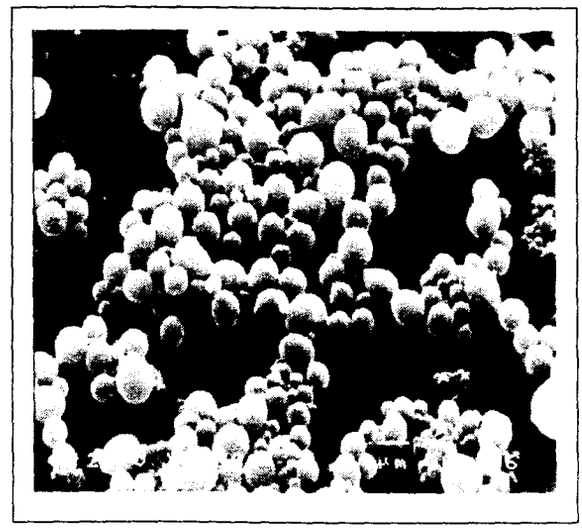

Figure 4.5 SEM Micrograph of PS1 preserved latex

4.3.2 SEM analysis of membrane surface morphology

Figure 4.6 shows the surface morphology of the active membrane layer of unused membrane FP110 using SEM analysis. At a magnification of 20.000 times. the SEM photo is fuzzy with black dimples indicating membrane pores. Although the black dimples were somewhat seen to be uniformly distributed. there were presence of varying sizes of the black dimples which indicates some form of none uniformity in pore size still exist. This could be one of the set-backs of using this type of membrane. No attempt was made to measure the pore size using SEM technique.

Figure 4.6 SEM surface morphology of FP110 membrane

4.4 Hydraulic resistance of the membrane R_m

As discussed in Chapter 2 (see section 2.15.2.1) theoretically permeate flux varies directly to the TMP which enables L_P (the pure water permeability of the fresh membrane) to be obtained from the slope of the corresponding permeate flux-TMP graph of water test done for PVDF (100kD MWCO) membrane. The plot of water flux tests versus TMP for chemically cleaned membrane before the start of experiments is as shown in Figure 4.18 (Mem-01-00) and Figure 4.21 (Mem-03-00). From the average value of the gradients of these graphs the value of L_P was calculated to be 1.38E-05m^3/s.m^2.bar (49.84L/ m^2.h.bar).

$$R_M = 1/(\mu . L_P) \qquad (2.5)$$

By using equation (2.5) and substituting 1.38 x 10^{-5} m^3/s.m^2.bar for the value of L_P and 2.88 $kg^{-1}h^{-1}$ for the viscosity of water at 30 C the value of R_m was calculated to be 69.98 h^2.m/L.

The supplier of this membrane, PCI Limited UK did not give an expected value for R_m for this membrane for comparing purposes.

4.5 Evaluation of suitable preservation system

A total of four test runs were performed with two runs using preservation system PS1 and 2 runs with preservation system PS2. The raw data (1, 2, 3 and 4) are tabulated in Tables A-1, A-2, A-3, and A-4 in Appendix A for samples references of DV/UF/4, DV/UF/5, DV/UF/6 and DV/UF/7.

4.5.1 Evaluation of preservation system PS 1

The sample DV/UF/4 with preservation system PS 1 was allowed to undergo maturation for 3 days before the UF run begun. During manual sieving the amount of coagulum collected was 5.4g per 20 kg (30% DRC) mass of the latex sample. This works out to be only 0.09% loss in dry weight of the sample as coagulum. This is an indication that no premature coagulation had taken place before the run from the sample that was prepared 3 days earlier.

During the test run the latex remained stable even at a maximum TMP of 6 barg, as there were no blockages along the pipe or at 200μm Y- strainer of the UF system. Jamming of feed pump was also not encountered. There was quite an amount of foaming during the recycling of the retentate into the feed tank. The foaming was due to the release of ammonia from the latex as the temperature of the day rose. The diaphragm pump caused pulsation, which made the pressure gauges to oscillate rapidly. Great care was taken to obtain the correct TMP from the readings of pressure gauges. The lowest TMP attained was only 2.5 barg as lower values of TMP were

difficult to establish due to the rapid oscillation of the pressure gauges and intense vibration of the whole UF system.

From Figure 4.7 it can be seen that at low-pressure readings (TMP < 3 barg) the flux increased very gradually with TMP and reached a maximum of 2.94×10^{-6} $m^3/s.m^2$ at 2.75 barg and slowly decreased and reached the lowest value of 1.29×10^{-6} $m^3/s.m^2$ at 5.50 barg. This was due to concentration polarization and cake layer being formed at the membrane wall. Decrease in flux can also be partly attributed to membrane compaction at high TMP.

Results of total protein content (TPC) analysis for sample DV/UF/04 using preservation system PS1 is as shown in Table 4.2. The maximum TPC value for the permeate was obtained. at a TMP value of 4 barg which is 3138 µg/g. These rather high values imply that the preservation system PS1 was very effective as it was able to maintain the protein from undergoing degradation into volatile fatty acids.

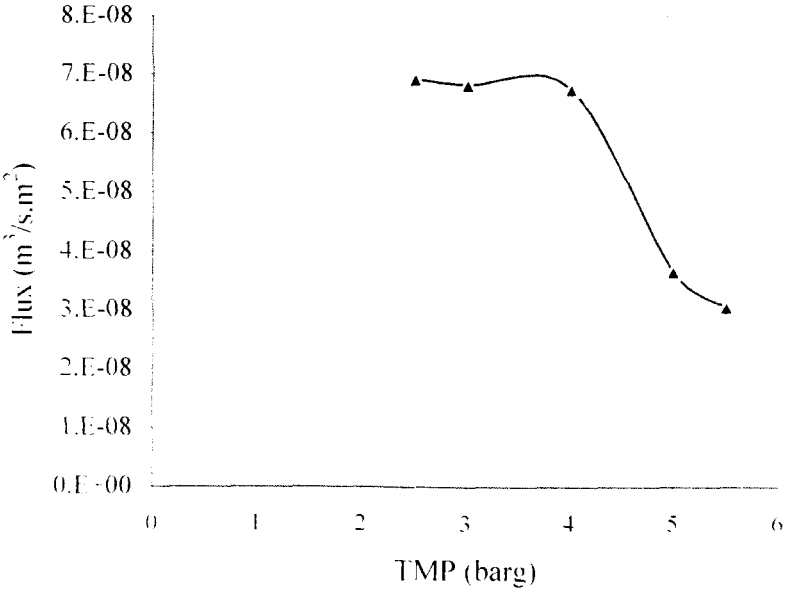

Figure 4.7 Graph of flux against TMP for sample reference DV/UF/04

Table 4.2 TMP, Permeate Flux, Volumetric cross flow rate and Protein Content values of Sample DV/UF/04

TMP (barg)	Calculated permeate flux J_V (m^3/s. m^2) x 10^{-6}	Volumetric cross flow rate (ml/s)	Protein content (µg/g)
2.50	2.94	253	2787
3.00	2.90	251	2186
4.00	2.87	197	3360
5.00	1.56	179	3138
5.50	1.30	131	2285

The repeat of this experiment was carried out using sample DV/UF/06. During the manual sieving the amount of coagulum collected were 11.4g per 20 Kg (30% DRC) mass of the latex sample. This works out to be only 0.14 % loss in dry weight of the sample as coagulum. Care was taken to obtain flux reading at as low TMP as possible so as to obtain a flux where membrane compaction was lowest. The lowest TMP attained was of 1.75 barg with a calculated flux of 4.78×10^{-6} m^3/ s. m^2. Further lowering of TMP value caused vigorous vibrations of the UF system and reading the pressure gauges became difficult. The maximum flux obtained in this experiment was 5.55×10^{-6} m^3/ s. m^2 at a TMP of 2.75 barg. Generally the permeate flux values obtained for sample DV/UF/06 as shown in Figure 4.8 were much higher for every corresponding values of TMP compared with sample of DV/UF/04 although the same membrane was used with cleaning. This may be due to more pores in the membrane being opened up during chemical cleaning process after the first UF run with latex sample as compared to the first cleaning before UF run.

During the UF run of sample DV/UF/06, the maximum permeate flux was obtained at a TMP of 2.75 barg which coincided with the maximum feed flow rate of 341ml/s. This fact best explains the important factor that the high flow rate increases the shearing action on the membrane, coupled with the turbulent flow and pulsating action of the diaphragm pump, which prevented the formation of the cake layer to some extent thus increasing permeate flux.

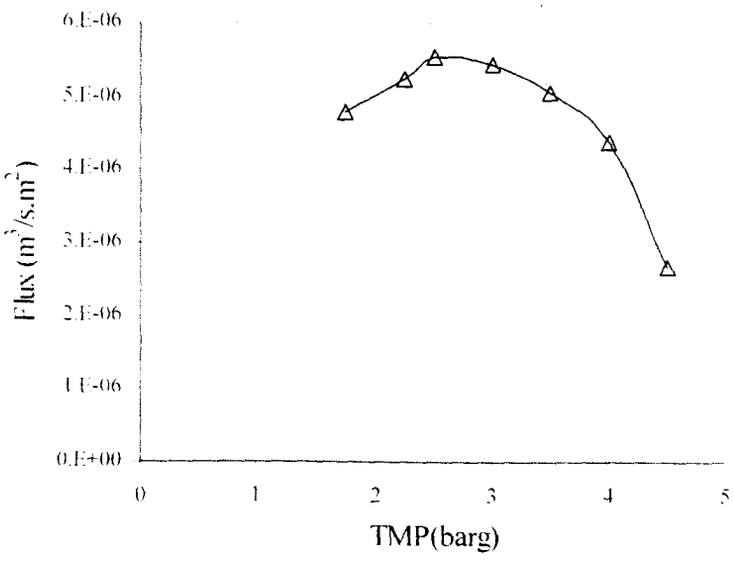

Figure 4.8 Graph of flux against TMP for sample reference DV/UF/06

Table 4.3 TMP. Permeate Flux.Volumetric cross flow rate and Protein Content values of Sample DV/UF/06

TMP (barg)	Calculated permeate flux J_V ($m^3/s.\ m^2$) x 10^{-6}	Cross flow rate (ml/s)	Protein content (µg/g)
1.75	4.78	313	3403
2.25	5.23	327	2975
2.50	5.55	341	3176
3.00	5.44	336	2789
3.50	5.07	307	2575
4.00	4.37	295	3052
4.50	2.68	222	2586

4.5.2 Evaluation of preservation system PS2

Samples DV/UF/05 and DV/UF/07 were prepared using preservation system PS2. While sieving the samples before the run, the mass of coagulum retained on the wire mesh was much higher at 57.2g and 63.9g respectively. These values were 10 times higher compared to latex using preservative system PS1. A slight malodour was detected coming from this NR latex, which was an indication of the formation of VFA that might lead to destabilization of the latex sample.

Foaming in the feed tank during recycling of the retentate was much less compared to with PS1 as the ammonia used was only 0.6%.

The Flux-TMP graph for sample DV/UF/05 is given in Figure 4.9 where the maximum flux of 4.77 x10^{-6} m^3/ $s.m^2$ was obtained at a TMP of 1 barg. Lower TMP than that obtained with PS1 runs (DV/UF/04 and 06) was achievable, although TMP less than 1 barg was again difficult to maintain, as the system vibrated very strongly and the reading on the pressure gauge was virtually impossible to read.

The results of total protein content (TPC) for sample DV/UF/05 is given in Table 4.4. It can be seen that both methods of TPC determinations show the same pattern with values decreasing with an increase in TMP. The maximum TPC value of permeate was obtained at 1 barg which were 1506 μg/g by the OVBM Method.

During the UF run with sample DV/UF/07, the 200μm Y-strainer became blocked and the run was interrupted and resumed after the strainer was cleaned of blocked rubber. The blocking of the strainer was due to small pieces of coagulum in the feed which formed a big lump on the mesh of strainer thus blocking the passage of the feed.

The Flux-TMP graph for sample DV/UF/07 is given in Figure 4.10 where a maximum flux of 4.54×10^{-6} $m^3/s.m^2$ was obtained at a TMP of 1.75barg, which coincided with the maximum flow rate value of 322 ml/s. This observation further supports the fact that high flow rate increases the shearing action.

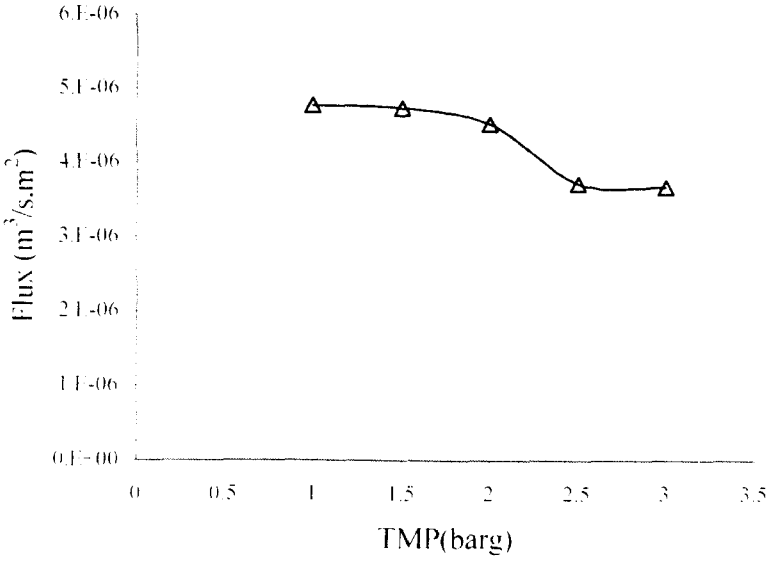

Figure 4.9 Graph of flux against TMP for sample reference DV/UF/05

Table 4.4 TMP, Permeate Flux, Volumetric cross flow rate and Protein Content values of Sample DV/UF/05

TMP (barg)	Calculated permeate flux J_V ($m^3/s.\ m^2$) x 10^{-6}	Volumetric cross flow rate (ml/s)	Protein content (µg/g)
1.00	4.77	320	1506
1.50	4.73	288	1438
2.00	4.52	270	921
2.50	3.70	266	658
3.00	3.67	250	579
3.50	3.18	200	493
4.00	2.24	158	434

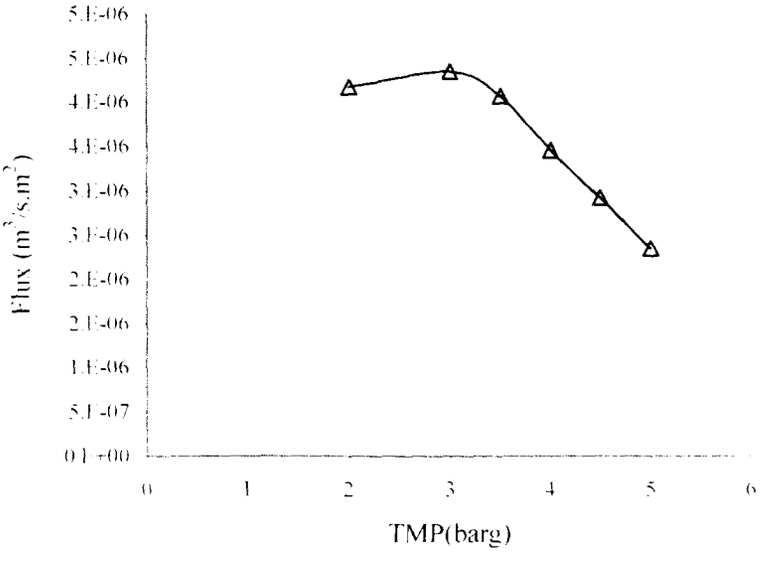

Figure 4.10 Graph of flux against TMP for sample reference DV/UF/07

Table 4.5 TMP, Permeate Flux, Volumetric cross flow rate and Protein Content values of Sample DV/UF/07

TMP (barg)	Calculated permeate flux J_V ($m^3/s.\ m^2$) x 10^{-6}	Cross flow rate (mL/s)	Protein content (µg/g)
1.75	4.54	308	1883
2.20	4.16	322	1685
3.00	4.34	312	1379
3.50	4.06	310	751
4.00	3.45	290	798
4.50	2.91	251	626
5.00	2.35	218	728

4.5.3 Selection of preservation system

Preservation system PS1 was found to be more effective then PS2 as the latex was more stable. The fact that it was more stable was made evident by the smaller mass of coagulum retained on the sieving mesh during manual sieving before the UF runs. Using this preservation system there was no blockage of the strainer of the UF system. During handling of the latex there was no malodour generated similar to the case of PS2.

It was also observed that using system PS2, maximum permeate flux was obtained at much lower TMP compared to using system PS1. This could be because higher level of ammonia in the gaseous form was released from the latex as the temperature in laboratory increases using system PS1 causing some frothing in the feed tank. This in turn caused the system to vibrate vigorously making reading of the pressure gauges at lower TMPs difficult.

The TPC values (Tables 4.2 and 4.3) for PS 1 (Samples DV/UF/04 and DV/UF/06) were rather high compared to TPC (Tables 4.4 and 4.5) of PS 2 (Samples

DV/UF/05 and DV/UF/07). The TPC values for system PS2 decreased sharply with increase in TMP. The generally high values of TPC with preservation system PS1 showed that the NR latex remained stable and able to arrest any microbial degradation of latex protein. It can be concluded that the high TPC values with lesser amount of coagulum during manual sieving coupled with the absence of any blockages at the Y-strainer of UF system makes PS1 the better preservation system compared to PS2. Since it was clearly identified that preservation system PS 1 is a better system, further UF experimental runs were conducted using system PS 1.

4.6 Effect of feed flow rate and TMP on permeate flux

This study was carried out using NR latex sample reference DV/UF/09 and procedure as stated in Experiment UF2. The experimental raw data 5 is shown in Table A-5 Appendix A. A plot of variations of permeate flux against filtration time at different TMP is given in Figure 4.11

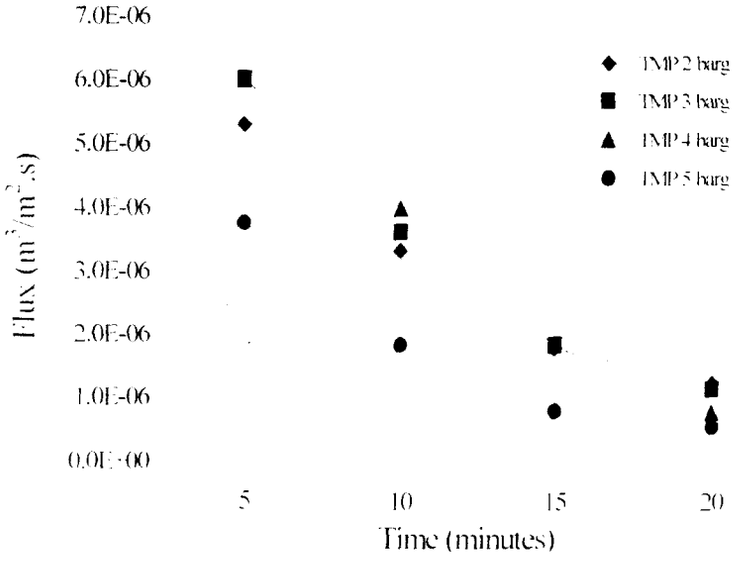

Figure 4.11 Variations of permeate flux against filtration time at different TMP

From the figure it can be seen that as expected the permeate flux decreases with time for every TMP. The decrease was most prominent at the high TMP of 5 barg and the least at intermediate TMP of 3 barg. These observations occurred in the pressure-controlled region. Deviation from this phenomena appeared at high TMP value. As can be seen from Figure 4.11 at 5 barg, when the TMP was at its highest value, the permeate flux was at its lowest value.

Reduction in flux occur by one of the two mechanisms: one being increase in the solid concentration on the membrane surface that results in a higher osmotic pressure, causing a decrease in the driving force (P_T-$\Delta\pi$) and flux. Osmotic pressure is generally valid for reverse osmosis of small molecules in solutions, but for UF and MF, the effect may still be prominent within the polarized layer and could become important if the solute concentration is high enough [22, 23]. This is because of the importance of the second and third viral coefficient in the osmotic pressure equation. The alternate view is that the high TMP acts against the cake layer compacting and blocking the pores of the membrane, thus the value for Rc from equation (2.4) increases and subsequently flux decreases.

A plot of variations of feed flow rate against TMP at different filtration time is given in Figure 4.12. From Figure 4.12 it can be seen that the feed flow rate is inversely proportional to TMP, and is the highest for the first 5 minutes for all the TMPs and shows the maximum value for the lowest TMP i.e., 2 barg.

TMP was basically the required backpressure for the feed to be filtered while passing across the membrane in cross flow filtration. As the TMP increases, the feed flow rate subsequently decreases. This, in turn causes less shearing action against the

membrane, resulting in the formation of cake layer on the membrane wall and *Rc* to increase thus causing the permeate flux to decrease [22, 23].

High flow rate (feed velocity) would cause turbulence and high shear force on the membrane would sweep away accumulated latex particles, reducing the hydraulic resistance of the cake and reducing the thickness of the boundary layer. When the system was in the pressure controlled status, this effect was insignificant as the concentration polarization and cake built up on the membrane surface was minimal. At higher TMP values the effect of velocity on the permeate flux was prominent. UF carried out at TMP values, of 3, 4 and 5 barg are known to be in the pressure independent regions. Figure 4.13 shows an increase in feed flow rate at these TMP values which prominently increased the permeate flux as shown from the slopes of feed flow rate ranging from 180ml/s to 360ml/s. Therefore, high feed flow rate increased permeate flux in the pressure independent regions.

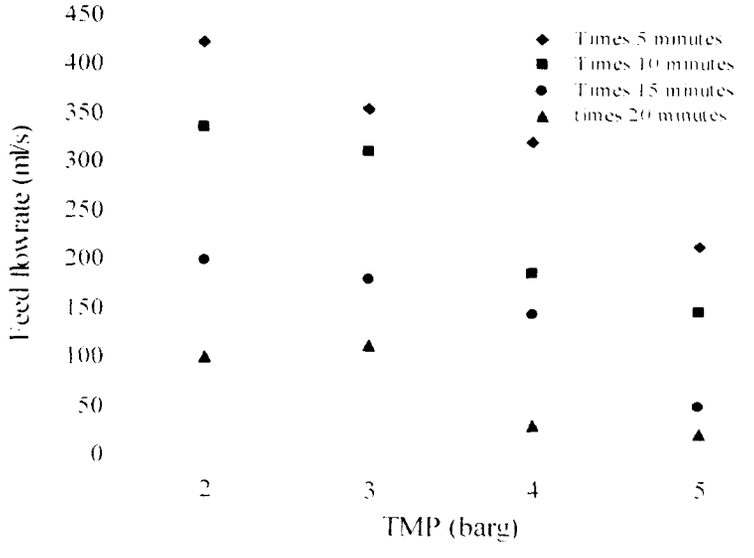

Figure 4.12 Variations of feed flow rate against TMP at different filtration time

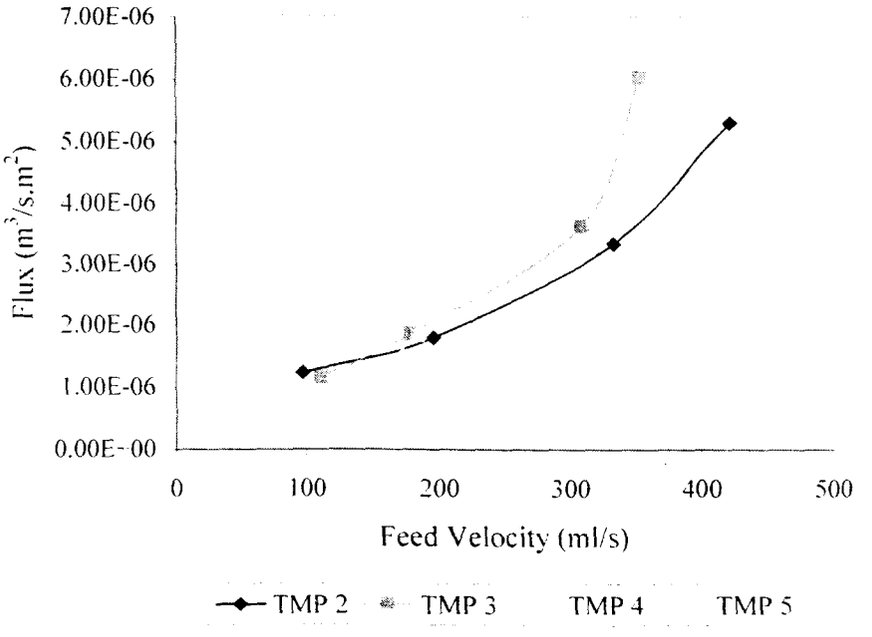

Figure 4.13 Variations of permeate flux with feed flow rate at different TMP

4.7 Optimum TMP for concentration process

This study was carried out using NR latex sample reference DV/UF/10 and repeated with sample reference DV/UF/11 and the procedure as stated in Experiment UF3. The experimental raw data 7 and 8 are presented in Table A-7 and A-8 in Appendix A.

A plot of variations of flux against TMP is given Figure 4.14. From Figure 4.14 it can be seen clearly that at low applied pressure the flux varies linearly with TMP until the flux reaches a maximum value, then it starts to decrease [20, 34]. The membrane was chemically cleaned before taking flux reading for a subsequent new TMP value, so that the value obtained for flux would be free of any cake layer interference from the earlier filtration. This is to prevent the gradual concentration of

solids on the membrane surface during stepwise increasing of TMP. This way it was expected to determine the critical flux [34].

Critical flux can be considered to be the flux just below that at which deposition onto the membrane to form a cake layer begins. At this point a concentration polarization layer was present but this does not become solidified into a cake on the membrane surface and in principal is reversible. Operating UF process at a permeate flux lower than or equal to critical flux could reduce or eliminate irreversible membrane fouling [34, 38]. Nevertheless, the *Rm* value from equation (2.4) for polymeric membrane (PVDF) is found to increase with increasing TMP and operating time due to membrane compaction [38]. This coupled with low feed flow rate at high TMP causes the *Rc* value to increase as well. Increase of *Rc* and *Rm* from equation (2.4) values cause the permeate flux to decline [22, 23, 38]. Therefore the ideal TMP for concentration is 2.75 barg below critical flux of $6x10^{-6}$ $m^3/s.m^2$ from Figure 4.13 and still in the pressure controlled region (< 3 barg).

A plot of variations of feed flow rate against TMP is given in Figure 4.15. Figure 4.15 clearly supports the fact that feed flow rate is inversely proportional to TMP or backpressure as stated in Section 4.6. From Figure 4.14 a TMP value of approximately 2.75 barg corresponds to a flow rate of 300 ml/s.

Therefore the ideal TMP for concentration should between 2.5 to 2.75 barg (below 3.00 barg) so as to be in the pressure controlled region.

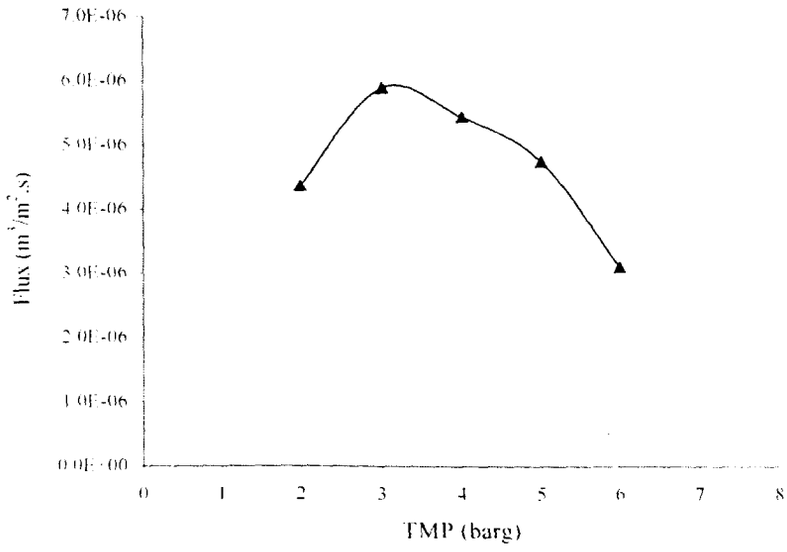

Figure 4.14 Variation of flux against TMP to determine optimum TMP for concentration process

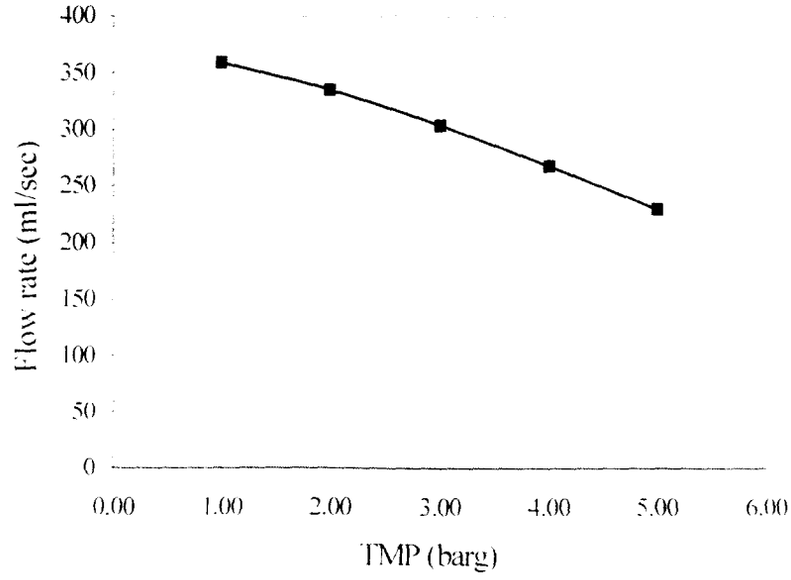

Figure 4.15 Variation of feed flow rate against TMP

4.8 Degree of concentration achievable

For this experiment sample reference DV/UF/12 was used with preservation system PS1 (Experiment UF2, UF3 and UF4). The applied pressure was adjusted until the TMP reached 2.75 barg. The concentration process was carried out 7 hours per day for 3 days covering a period of 20 hours. The system was run for 7 hours per day because the compressed air supply for the feed pump could only be obtained during the working hours of the Chemical Engineering Department Workshop (9.00 am to 5.00 pm).

The membrane was not chemically cleaned each day after the 7 hours of run. Once the retentate or concentrated latex was drained off from the system, it was rinsed with DI water with the pump turned on. At the end of the rinsing process the membrane was packed with DI water and left overnight. Chemical cleaning process was not carried out at the end of each day, because experiment UF4 was to evaluate the degree of damage and fouling of the membrane that could possibly happen. The following day, care was taken to completely drain off the DI water remaining in the pipes which could dilute the latex once the filtration was resumed the following day. The average rise in temperature was about 16°C for a 7-hour concentration run per day. The rise in temperature did not create any adverse effect to the stability of the feed. NR latex would remain stable up to a temperature of 60°C [1-4]. The feed remained stable when the highest temperature of 44°C recorded during a 7 hour run.

A plot of variation of permeate flux against time of concentration is as shown in Figure 4.16 while Figure 4.17 is a plot of the cumulative mass of permeate collected with time. This experimental run was conducted to evaluate the longest period the membrane could withstand fouling as well as the maximum concentration attained.

As can been from Figure 4.16 there was a gradual decline of the permeate flux for the first 15 hours and from the 18th hour onwards it reached a constant value. The final DRC analysis of the retentate after UF run for 20 hours gave a value of 46.09% from an initial DRC value of the feed of 29.61%. The increase in viscosity from 5.10 to 8.30 cP was the result of increase in DRC upon concentration and the effect is as mentioned in section 4.1.1.3.

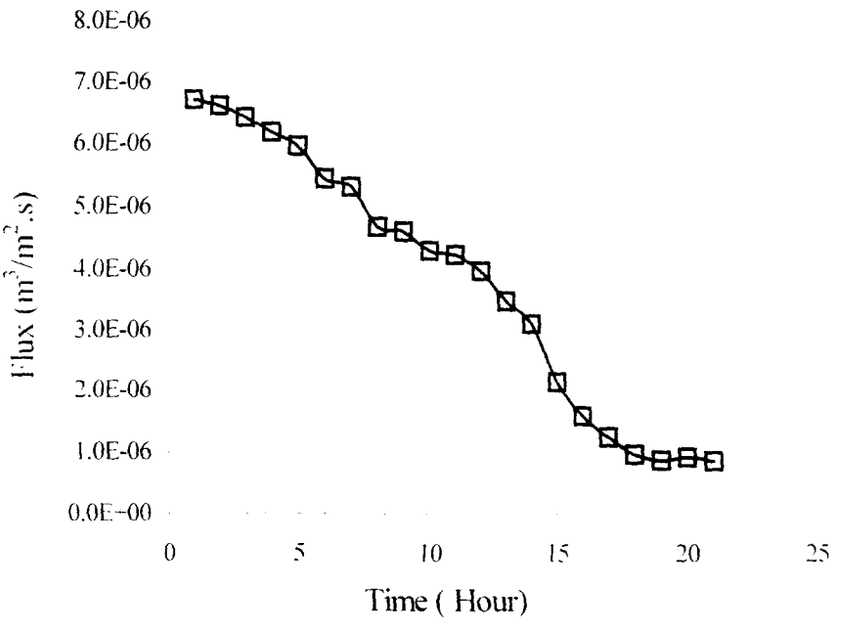

Figure 4.16 Variations of flux with time during concentration process

Table 4.6 shows DRC, TSC, pH and viscosity values before and after concentration and the experimental raw data 9 are presented in Appendix A. An average rise in temperature of about 16° C from an initial value of 28 °C was noted for a 7-hour concentration run per day.

Table 4.6 DRC, TSC, pH and viscosity values before and after concentration process.

Testing Parameters	DRC (% mass)	TSC (%mass)	pH	Viscosity (cPs)
Before UF run	29.61	32.09	10.41	5.10
After UF run (20hrs)	46.09	48.52	10.04	8.30

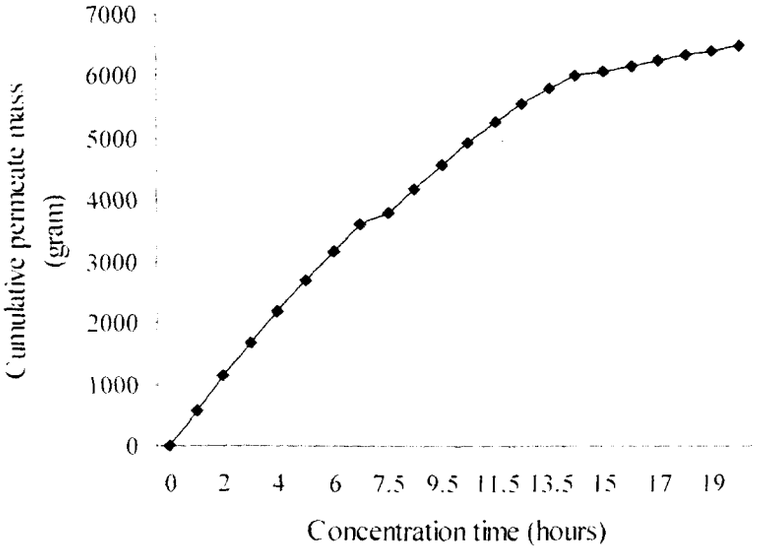

Figure 4.17 Cumulative permeate mass against concentration time

The concentration process was interrupted by the presence of DI water that was left in the system which could not be drained off completely. This water diluted the feed when the run resumed the following day. Some rubber was deposited at the pump's inlet ball valve. The initial DRC was calculated to be 29.61% and the final DRC was 46.09%. The calculation of percentage concentration per square meter per hour is as follows:

$$\frac{\text{Final DRC - Initial DRC}}{\text{Membrane area x Concentration time}} = \frac{(46.09 - 29.61)}{0.024 \times 20} = 34.97\% \, m^{-2} hr^{-1}$$

Taking the area of membrane to be $0.024m^2$.The increase in DRC value per square meter membrane area per hour (m^2/hr) was 34.97%.

The rinsing of the membrane with DI water could only remove the gel layer on the surface of the membrane whereas the membrane itself was being fouled continuously during the 20 hrs of UF run. The initial flux (J_V) of $6.71x10^{-6}$ $m^3s^{-1}m^{-2}$ dropped to $4.67x10^{-6}$ $m^3s^{-1}m^{-2}$ after eight hours of UF run. The 3 cycles of DI water rinsing could not improve the flux as the calculated flux value after the 1st hour of UF run was $4.60 x10^{-6}$ $m^3s^{-1}m^{-2}$ when the UF run resumed the following day. There was a drop of 31% from the initial flux value after 8 hours of UF run. After a 20 hours of UF run the final flux was calculated to be of $8.61x10^{-7}$ $m^3s^{-1}m^{-2}$ which was a drop of 87% from initial flux value.

The alternative objective of Experiment UF4 was to obtain the worse condition that would lead to membrane fouling. The flux that was reduced to about 13% of its initial value was the result of severe fouling of the membrane, as washing with DI water could only remove the gel layer on the surface of the membrane. The NRL protein which has a molecular weight distribution ranging from 5kD to 50kD, coupled with the presence of macro molecules (100kD –200kD) which accounts for *ca.* 85% v/v of the total dispersed rubber, could have easily blocked up the pores of hydrophobic PVDF membrane wall.

The flux reduction was also partly due to increase in viscosity of the permeate. The permeate consists of water, carbohydrates resins and proteins. Higher molecular-mass and more viscous portions come at later stage of the filtration thus, flux drops.

4.9 Water flux test results

Water flux tests were conducted just before the commencement of an UF run. For unused membranes, water flux tests were carried out after preservative chemicals coated on the membrane surface had been removed as described in section 3.7.2 For a used membrane that was cleaned and kept wet by packing with cleaning solutions overnight, the solution was drained and replaced with DI water for water flux test to be carried out. Hydraulic membrane permeability, L_P (HMP) values, which can be obtained from the slope of water flux versus TMP graphs, were used to evaluate the cleaning efficiency of the membranes as shown in equation (4.1) below

$$J_r = [L_{p(c)} / L_{p(u)}] \times 100 \qquad (4.1)$$

Where: J_r = Percentage Flux Recovery

$L_{p(u)}$ = hydraulic membrane permeability value of new and cleaned membrane

$L_{p(c)}$ = hydraulic membrane permeability value of used and cleaned membrane

From the results of water flux tests shown in Table 4.7, for Mem-01-01 (Figure 4.19) there was a flux recovery value of 82%. That was an acceptable value (loss of < 20%) whereas for Mem-01-02 (Figure 4.20) an increase of 138% of flux recovery. This could be the result of membrane matrix rupture or bleed. After performing the 1st and 2nd UF runs with NRL respectively and undergoing the 2nd and 3rd cycles of chemical cleaning, the skin layer of asymmetrical membrane could have ruptured and caused the increase in hydraulic membrane permeability (HMP) value. The HMP values were much higher compared to undamaged membrane (Mem-01-00 and Mem-01-01). For subsequent experiments, after performing chemical cleaning the

membranes were not soaked with cleaning solution overnight, instead, DI water was used for the soaking and wetting purposes. According to the manufacturers specifications, the membrane functions best at pH range from 1.5 to 10.5 but pH of PS1 preserved latex at times exceeds 10.5. The damage to the membrane matrix could be due to the long duration of contact with high pH value of ammonia of the feed of NR latex, coupled with prolonged contact with cleaning solutions of 0.2% of NaOH. For subsequent experiments, care was taken to limit the pH of the feed not to exceed 10.5.

Table 4.7 Water Flux test Results

Membrane reference for water flux test	Figure	Slope of water flux test graph. L_p ($m^3/s.m^2.bar$) x 10^{-5}	Flux recovery
1st new membrane after undergoing 1st chemical cleaning (Mem-01-00)	4.18	1.44	100
1st membrane after 1st run with NRL after twice undergoing chemical cleaning (Mem-01-01)	4.19	1.18	82
1st membrane after 2nd run with NRL after trice undergoing chemical cleaning (Mem-01-02)	4.20	1.99	138
3rd new membrane after undergoing 1st chemical cleaning (Mem-03-00)	4.21	1.33	100
3rd membrane after 1st run with NRL and twice undergoing chemical cleaning (Mem-03-01)	4.22	1.23	93
4th new membrane after undergoing 1st chemical cleaning (Mem-04-00)	4.23	1.40	100
4th membrane after 20 hrs run with NRL (Mem-04-01) after twice undergoing chemical cleaning	4.24	1.21	86

Experiment UF4 was to determine the degree of concentration achievable. After 20 hours of UF run the membrane was fouled. The 3 cycles of rinsing with DI water followed by 1 hour of chemical cleaning of membrane was not able to restore to about 86 % of the initial HMP value. HMP value dropped from an initial value of 1.41E-05 [4th unused membrane (Mem-04-00), Figure 4.23] to a 1.21E-05 [same membrane after 20 hours UF run with latex (mem-04-01), Figure 4.24]. The cleaning procedure employed was effective as the HMP recovery value was well above recommended value of 80%. The membrane could still be kept for further use value [25].

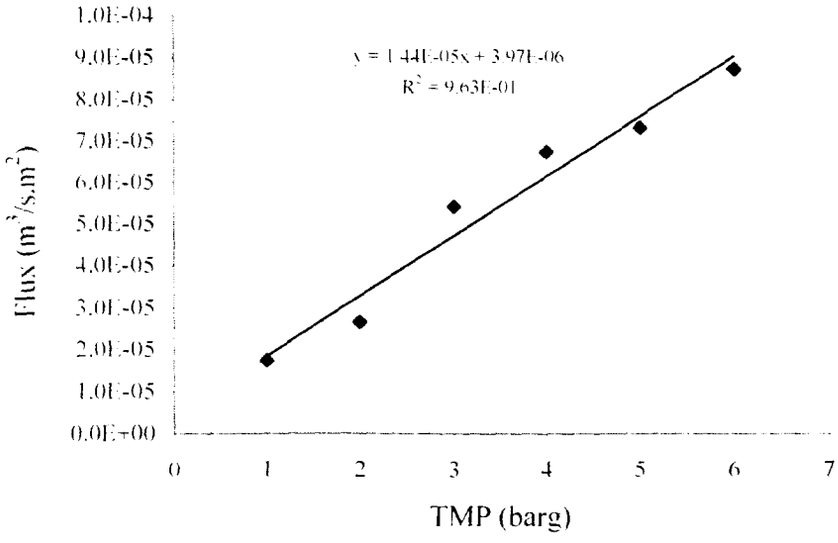

Figure 4.18 Water flux test result obtained for the 1st unused membrane after completing 1st chemical cleaning (Mem-01-00)

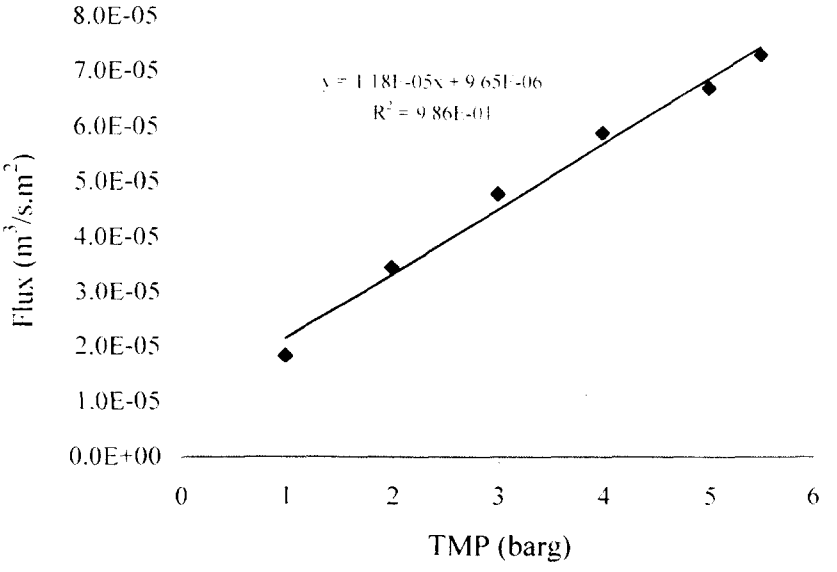

Figure 4.19 Water flux test result obtained after membrane was cleaned for the 2nd time after 1st UF run utilizing NRL sample DV/UF/04 (Mem-01-01).

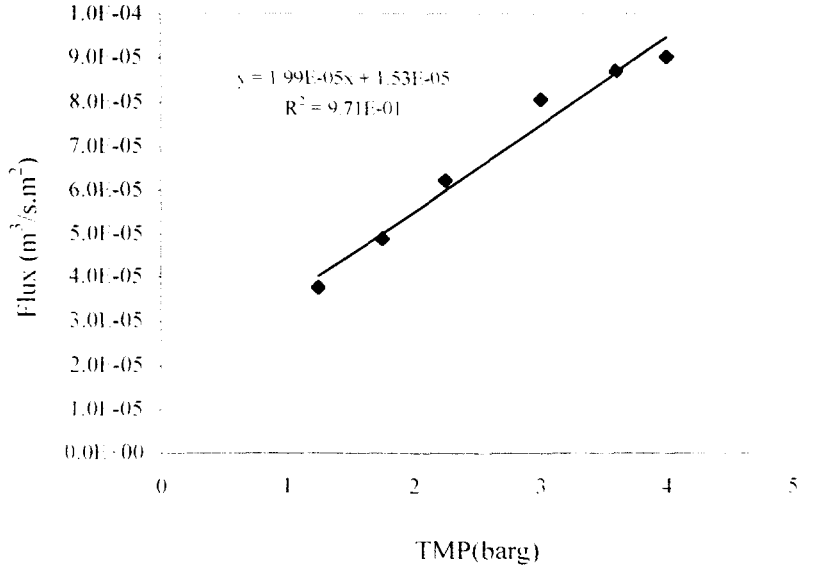

Figure 4.20 Water flux test result obtained after membrane was cleaned for the 3rd time after 2nd UF run utilizing NRL sample DV/UF/05 (Mem-01-02).

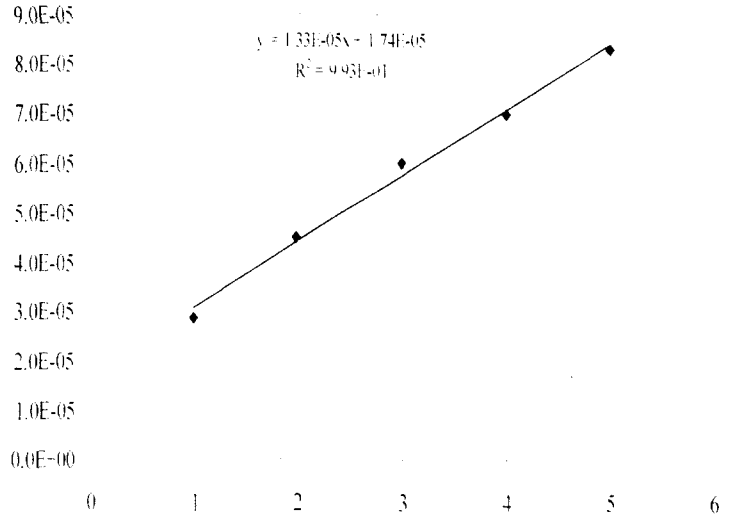

Figure 4.21 Water flux test result of 3rd unused membrane after cleaning it from membrane preserving chemicals (Mem-03-00)

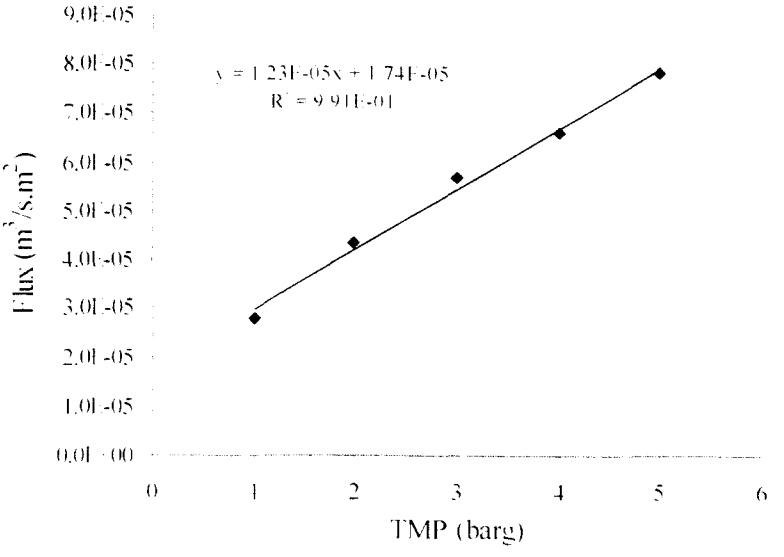

Figure 4.22 Water flux test result obtained after membrane was cleaned for the 2nd time after 1st UF run utilizing NRL sample DV/UF-10 (Mem-03-01)

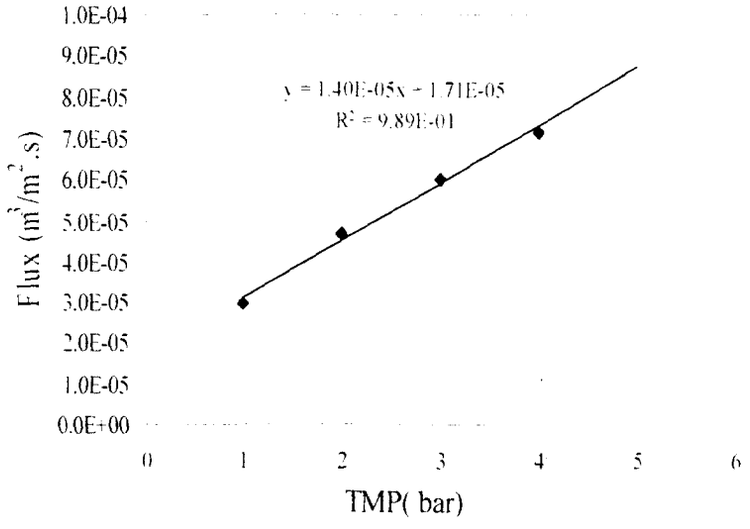

Figure 4.23 Water flux test result of 4th unused membrane after cleaning it from membrane preserving chemicals (Mem-04-00)

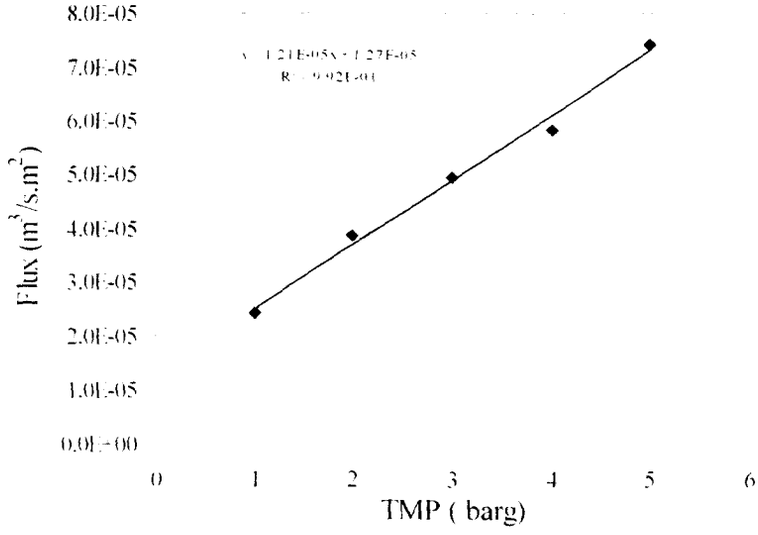

Figure 4.24 Water flux test result of a membrane after 20 hrs of UF run and undergoing chemical cleaning procedure (Mem-04-01)

4.10 Flux recovery

The membrane cleaning procedure as mentioned in section 3.7.3 was able to make flux recoveries of 81.73% (Mem-01-01), 92.68% (Mem-03-01) and 86% (Mem-04-01) respectively after the UF runs with NR latex. The flux recovery results were all above 80% which imply that the membrane still could be used for further UF runs [25]. Water flux test done on membrane Mem-04-00 which was used for UF run for concentration process for 20 hours gave a flux recovery of 86% after under going cleaning procedure (Mem-04-01).

From the results of the flux recovery, the cleaning procedure was satisfactory although the procedure could not completely eradicate the permanent fouling of the membrane. NR latex is a natural colloid and its constituents besides latex hydrocarbon are lipids and macro-molecular protein which could easily foul the membrane. As the molecular weight of rubber in NRL ranges from 30kD to 200kD, the smaller rubber particles could also be a factor causing permanent fouling of the membrane. Chemical cleaning procedures for protein fouling, as well as finding suitable method of overcoming blocked membrane pores by smaller sized latex particles need to be investigated. This would prolong the economic life span of a membrane involved in the process of concentrating NR latex.