

Concentration of Natural Rubber Serum by Reverse Osmosis

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A preliminary investigation was made into the well-known process of reverse osmosis (RO) for its possible use to concentrate the serum (NRS) that is derived from the coagulation of various types of natural rubber latices. The results showed that concentrated NRS with a maximum total solids content of about 12% (w/w) could be obtained using up to 50 bars of pressure. The maximum concentration factors obtained were about 3.8 whilst the maximum recoveries were around 87%. Membrane fouling and the poor quality of the resultant permeates which were also observed suggest that the aromatic polyamide membrane material used in the RO equipment was not suitable for NRS.

The result of a collaborative effort between the RRIM and the Yokohama Rubber Company (YRC) of Japan first initiated in 1987 was the development of a process for the recovery and concentration of the aqueous portion of natural rubber latex, otherwise termed natural rubber serum (NRS)¹. The process has subsequently been commercialised by a joint venture Malaysian-Japanese company, MYFEC, whose factory today plays an important role in solving the skim NRS effluent disposal problem of several latex concentrate factories which arises from the by-product skim latex. The concentrated NRS obtained is disposed off by MYFEC through conversion into a very effective and high-value organic fertiliser².

The present process for concentrating the NRS adopted by MYFEC is based on evaporation under reduced pressure. The energy requirement for this process is very high despite the innovative use of thermal vapour recompression and the re-cycling of the vapour³. Inevitably, the energy costs go up considerably with increasing amounts of water to be evaporated, or in other words, with

decreasing total solids content (TSC) of the NRS used. The process, not surprisingly, is therefore at present economically restricted to skim NRS, which has a TSC much higher than those of NRS derived from block rubber coagulation. Consequently, a major shortcoming of the process is that it cannot be applied to solve the pollution problem of all rubber processing factories.

Reverse osmosis (RO) is a membrane process which has been generally well-recognised and adopted for the desalination of water in arid regions⁴. Basically, it is a process whereby a solution of a salt or a low molecular weight solute is contacted with a membrane and is subjected to pressure so that a solution lower in solute concentration emerges from the other side of the membrane. The pressure that is applied must be greater than the difference in osmotic pressures of the solutions adjacent to the interfaces of the membrane in order to reverse the normal osmotic flow from the low to the high concentration side⁵. Being a low energy-demanding process, especially when used on solutions of low concentrations,

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RO was suggested as a possible alternative method for the concentration of NRS, in particular, those derived from block rubber processing factories. A laboratory RO unit was acquired by the RRIM in 1992 through YRC for such investigations. The results of those studies are presented in this paper.

THEORETICAL BACKGROUND

When solutions of different solute contents are placed adjacent to each other, solute diffuses between the two until a uniform concentration results. If, however, these two fluid phases are separated by a semi-permeable membrane, this route to equilibrium is blocked. (Semi-permeable membranes by definition are impermeable to solutes but transport solvent readily.) Instead, solvent is transferred in an attempt to dilute the solute content of the more concentrated solution – this process is called osmosis. Another equilibrium can be reached by establishing a pressure on the solution phase, called the osmotic pressure (π), which exactly balances the reduction in the chemical potential of the solvent caused by adding solute. This leads to the following thermodynamic definition of osmotic pressure for a solution:

$$\pi = - \frac{RT}{V_1} \ln(a_1) \quad \dots 1$$

where V_1 = Solvent molar volume
 a_1 = Activity of solvent in the solution
 T = Absolute temperature
 and R = Universal gas constant.

For dilute, ideal solutions, the above equation can be simplified and replaced by the van't Hoff relation, as follows:

$$\pi = \frac{RTC}{M} \quad \dots 2$$

where C = Concentration of the solute in the solution

M = Molecular weight of the solute
 T = Absolute temperature
 and R = Universal gas constant.

This equation can be readily used to calculate the osmotic pressures of dilute solutions of simple solutes. For sodium chloride (NaCl) in water for example, each unit increase in NaCl weight percent raises π by 700 kPa or *ca.* 7 atm. For macromolecular solutions, osmotic pressures are much lower; *e.g.* for a 10% solution of a polymer with $M = 10^4$, $\pi = 70$ kPa.

To obtain the osmotic pressure of NRS by the van't Hoff equation, the value of M would have to be determined beforehand. However, since NRS is a multi-component solution and the proportions of the different components are not known, it is difficult to assign a representative value for M . One way of overcoming this difficulty is to obtain the value of M by experiment, such as by comparing the osmotic behaviour of different solutions of NRS against those of a known substance like NaCl, at the same concentration levels. The results of this determination have been obtained previously⁶, and show that the osmotic pressures of the NRS solutions were in general about one-third of those of the corresponding NaCl solutions at the same concentration level. This would imply that the driving pressures required to reverse the osmotic flow of solvent encountered in solutions of NRS would therefore also be roughly one-third the pressures needed for NaCl solutions of the same concentration.

In reverse osmosis, the membrane system allows permeate, or water in the case of aqueous solutions, to pass through it when subjected to a pressure greater than the osmotic pressure difference between the concentrated and dilute compartments. The membrane excludes large molecules and ions. The exclusion is normally

not 100%, and different membrane materials and compositions will give different exclusions. *Figure 1* shows the basic parameters involved in the RO process, viz.:

- Q_F = Feed flow rate
- C_F = Solute concentration in feed
- Q_P = Permeate flow rate
- C_P = Solute concentration in permeate
- Q_C = Concentrate flow rate
- C_C = Solute concentration in concentrate.

The mass balance equations involving the above parameters are as follows:

$$Q_F = Q_C + Q_P \quad \dots 3$$

$$Q_F C_F = Q_C C_C + Q_P C_P \quad \dots 4$$

If the definitions for the concentration factor (X) and the recovery ratio (R) are given by the equations:

$$X = \frac{C_C}{C_F} \quad \dots 5$$

$$R = \frac{Q_C C_C}{Q_F C_F} \quad \dots 6$$

Then, by manipulation of the above four equations, the following additional relationships can be obtained:

$$R = \frac{C_C(C_F - C_P)}{C_F(C_C - C_P)} \quad \dots 7$$

$$R = \frac{C_C - X C_P}{C_C - C_P} \quad \dots 8$$

$$C_P = \frac{C_C(1-R)}{(X-R)} \quad \dots 9$$

Since $C_C \geq C_F$, we can see that $X \geq 1$ and $R \leq 1$.

It then follows from *Equation 8* that $R = 1$ when $X = 1$, and this condition occurs only when there is no concentration of the solution by the process. In all other situations when there is concentration taking place, the recovery ratio will be < 1 .

EXPERIMENTAL

Block rubber (SMR) serum derived from coagulation of latex was obtained from the RRI Experiment Station factory in Sungai Buloh, whilst the skim serum used was derived from the Lee Latex factory at Gombak. NRS concentrate (NRSC) prepared by the evaporation process, which was diluted to an appropriate concentration before use, was supplied by MYFEC. Sodium chloride (NaCl) solution which was used for the initial calibration runs, as well as sodium hydroxide and calcium hydroxide (the chemicals used for neutralisation), were of reagent quality. All raw materials were pre-sieved through a muslin cloth and then through a 0.2 micron filter to remove any suspended particles before use.

The reverse osmosis equipment which was supplied by YRC was a pre-assembled unit from Mitsui Engineering & Shipbuilding Co., Ltd. The RO module (ROM) fixed in the unit was of the aromatic polyamide type, No: SW4-60PAF 4040, which had a spiral-wound element configuration and dimensions of 102 mm OD \times 1016 mm length. A photograph showing the overall equipment is given in *Figure 2*. The flow-chart for the operation of the RO unit, showing the location of the various important processing controls and parameters measured, is given in *Figure 3*. The initial settings of the valves before each run were as follows:

- Valve V_1 – fully open
- Valve V_2 – fully open

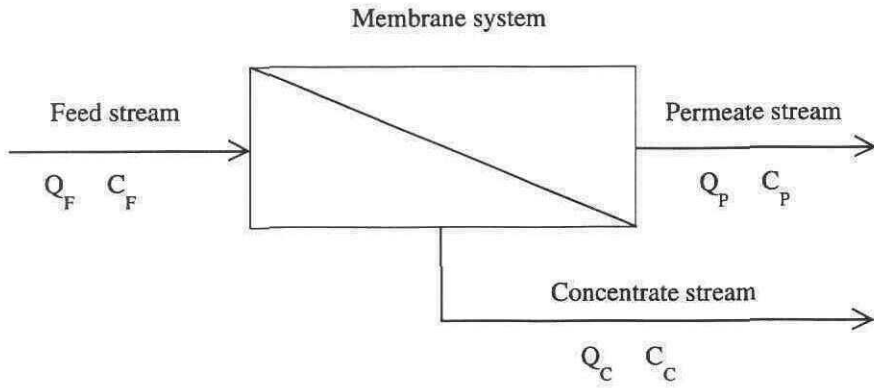


Figure 1. Basic parameters in reverse osmosis.

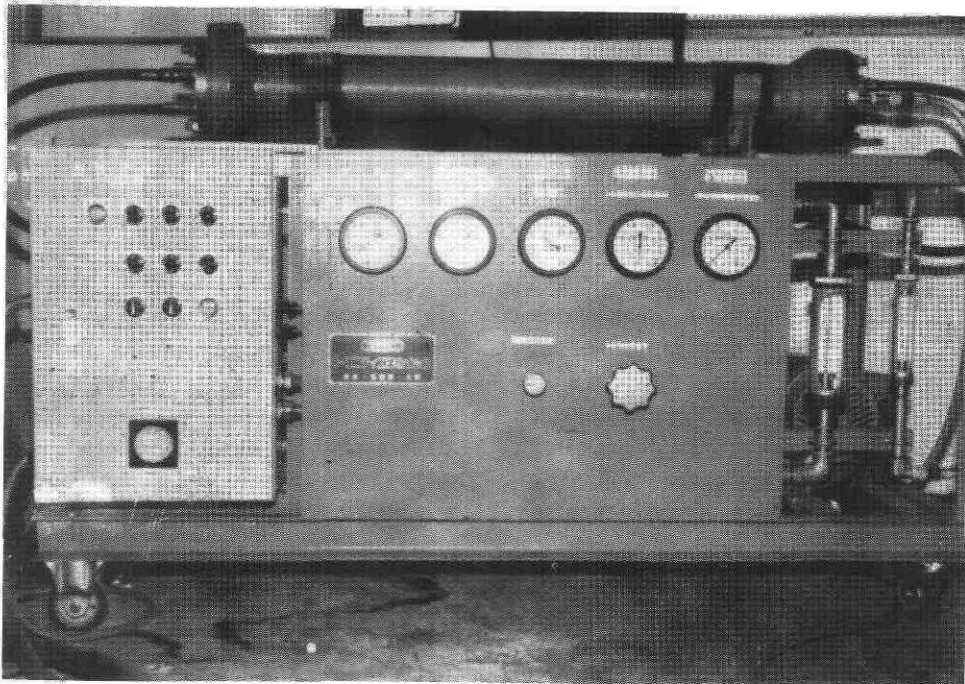


Figure 2. Reverse osmosis equipment for natural rubber serum.

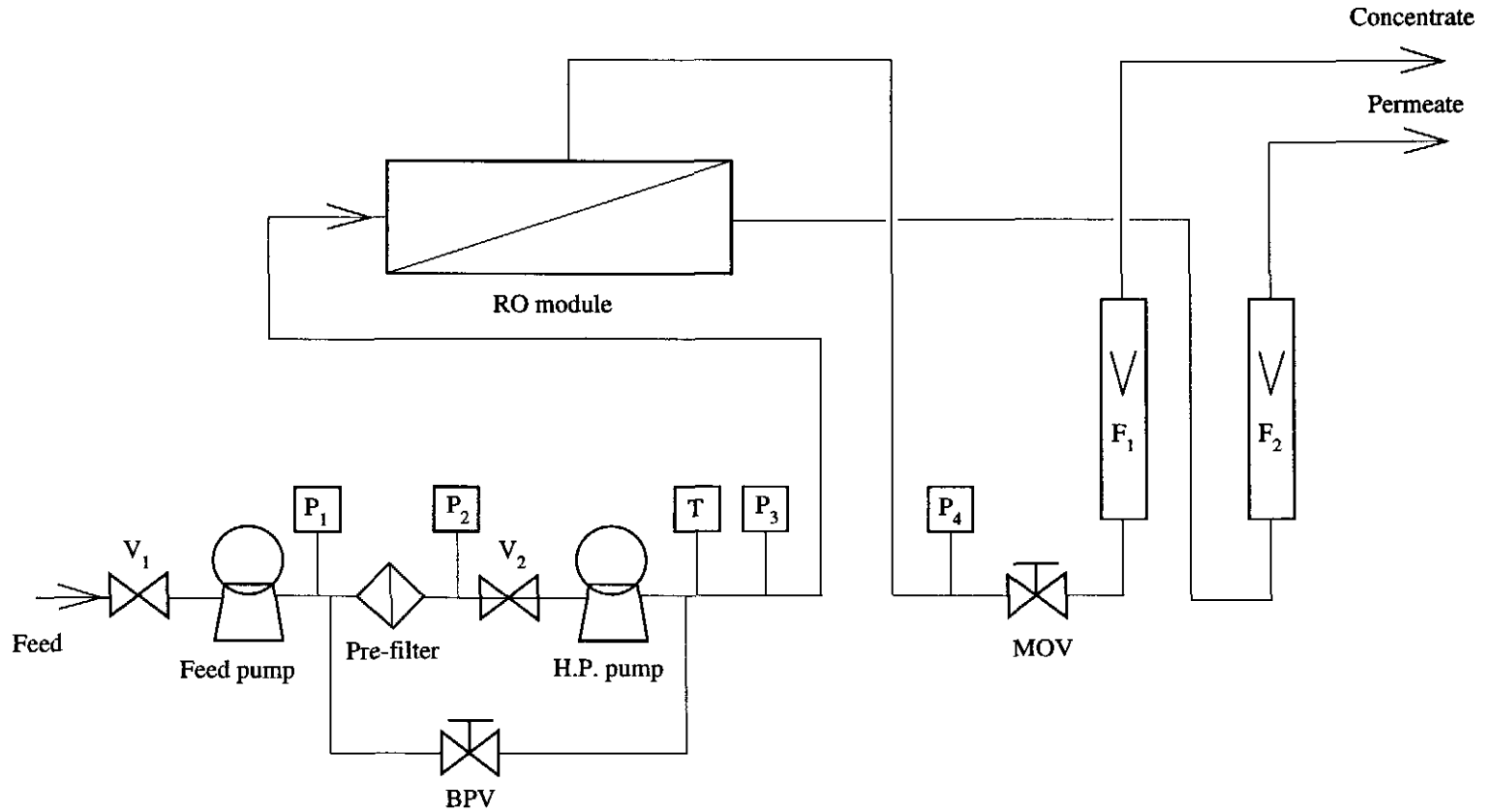


Figure 3. Flow-chart for reverse osmosis unit.

Module-operating valve (MOV) – fully open
 By-pass valve (BPV) – fully closed.

In a typical run, 100 kg of the raw material to be used was placed in a stainless steel feed tank (not shown in the flow-chart), and as soon as the feed pump was started, a timer was also started. Since the MOV was fully open, the initial material emerging from the concentrate outlet of the reverse osmosis module (ROM) was the same as the feed material, and was recycled to the feed tank. The various values of pressures (P_1 , P_2 , P_3 and P_4), temperature (T) and concentrate flow (F_1) were recorded. After one minute of running, the high-pressure (H.P.) pump was started, and the MOV was slowly closed so as to force part of the feed through the ROM which thus emerged from the permeate outlet. The MOV was adjusted until a reasonable initial flow (F_2) of about 2 litres/min of permeate was obtained. The permeate was collected in a separate container. After 2½ min from the start, the values of all the above parameters were again recorded, and this procedure was repeated thereafter at 5-min intervals of time until the equipment stopped (because of a high-pressure or high-temperature alarm condition) or when the permeate flow (F_2) became too low (below 0.5 litre/min). The amounts of concentrate and permeate obtained were then weighed, and their various properties tested. Total solids content measurements of the concentrate and permeate, as well as the measurements of permeate quality such as suspended solids (SS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were made according to the methods described in the manual on Laboratory Methods for Chemical Analysis of Rubber Effluent⁷. The values of concentration factor (X) and % recovery (R) for each RO run were obtained by calculation using the appropriate formulae.

RESULTS AND DISCUSSION

RO Test Runs using NaCl Solutions

NaCl solutions of various initial concentrations ranging from 1% (w/w) to 10% (w/w) were used. In all cases, the final concentration of the NaCl concentrate obtained was below 10% (w/w). In fact, when the 10% (w/w) solution was used as feed, no flow of permeate was obtained despite raising the pressure (P_3) until it exceeded the high pressure (H.P.) safety limit (of 65 bars). This result was not surprising in view of the high osmotic pressure of NaCl solutions, the values of which had been determined previously⁶. Figures 4 and 5 show the records of the various parameters which were monitored during the runs using the 1.0% (w/w) and 4.3% (w/w) solutions of NaCl respectively. Typically, as concentration of the solution took place, the module outlet pressure (P_4) and temperature (T) increased whilst the permeate flow (F_2) decreased. The concentration factor (X), which represents the amount of concentration achieved, was higher for the feed solution with the lower starting concentration; however, the % recovery of material (R), which represents the percentage of dry matter recovered as concentrate, was the opposite way round. The plot of the concentration factor against recovery for the NaCl runs (Figure 6) shows an inverse relationship, which implies that it is not possible to obtain both a high concentration factor and a high % recovery in the RO process at the same time.

RO Runs using Diluted NRSC

Diluted solutions of NRSC (obtained from MYFEC) were used as feed material after the preliminary runs with NaCl solutions. Not much problem was encountered in these runs, and the pressures required to produce similar permeate flows were much lower than those

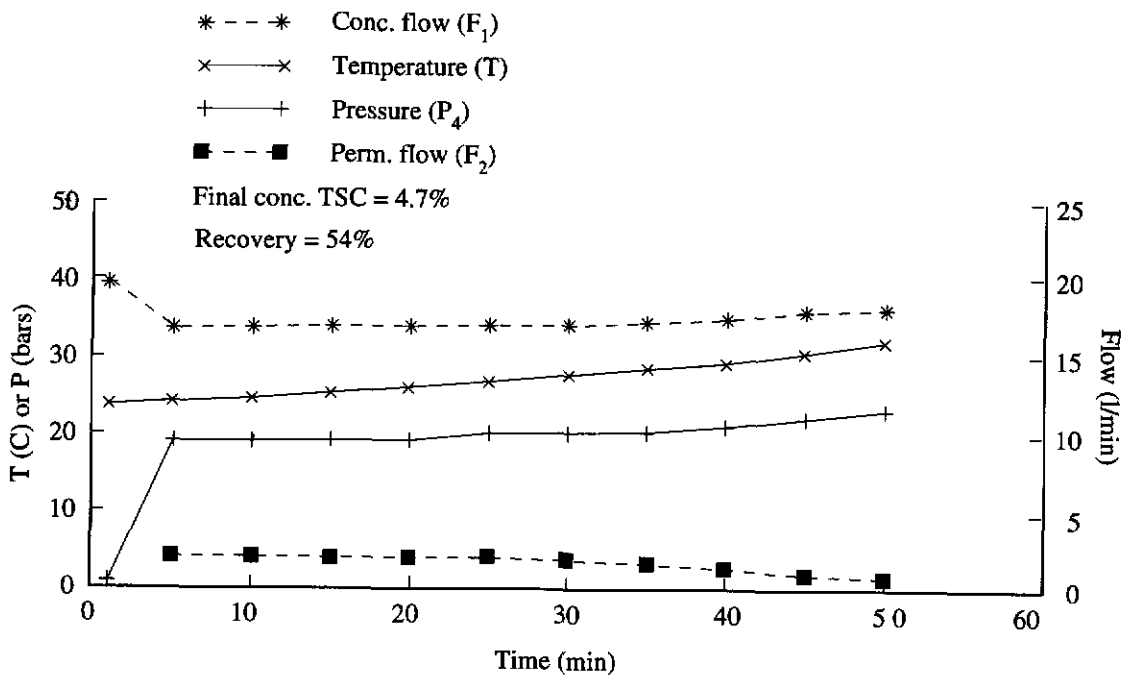


Figure 4. RO using NaCl solution (Initial TSC = 1.0%)

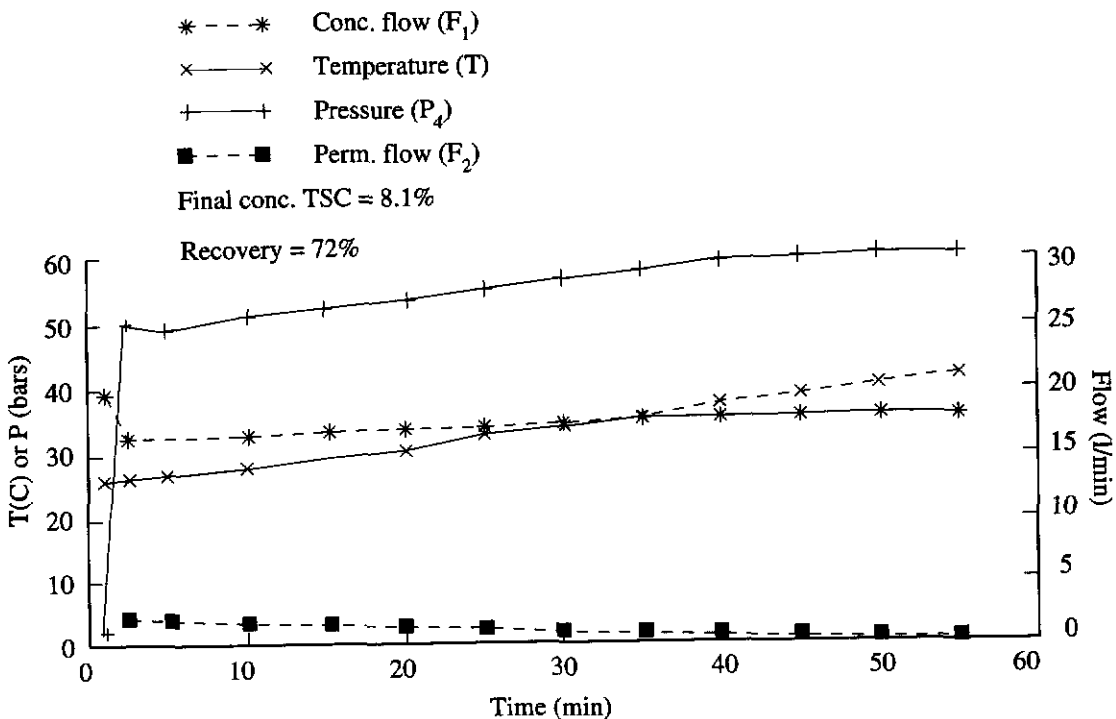


Figure 5. RO using NaCl solution (Initial TSC = 4.3%)

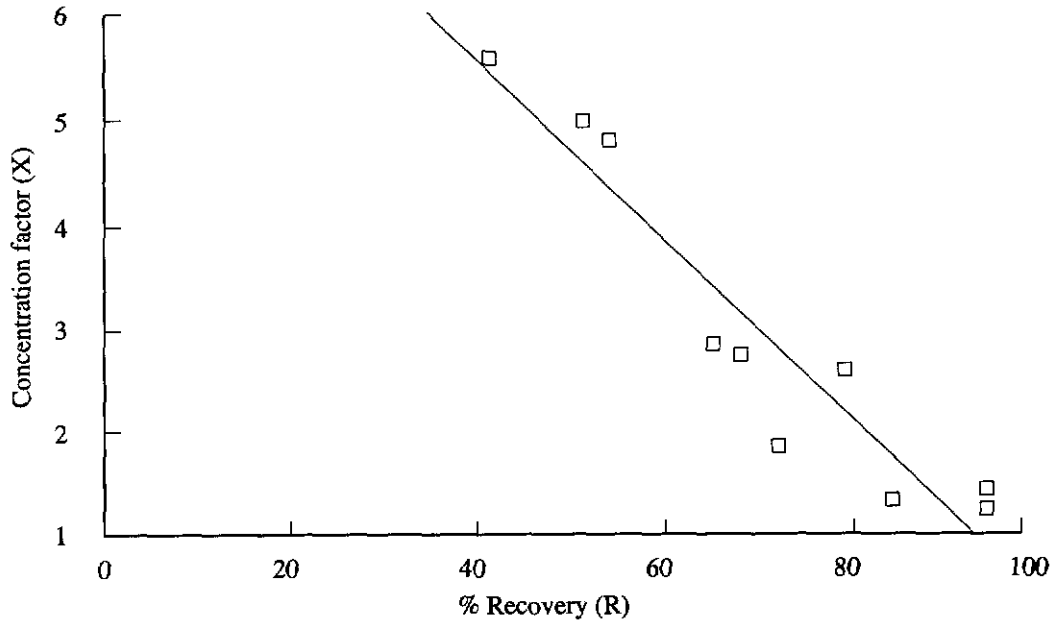


Figure 6. Analysis of RO runs with NaCl concentration factor versus recovery.

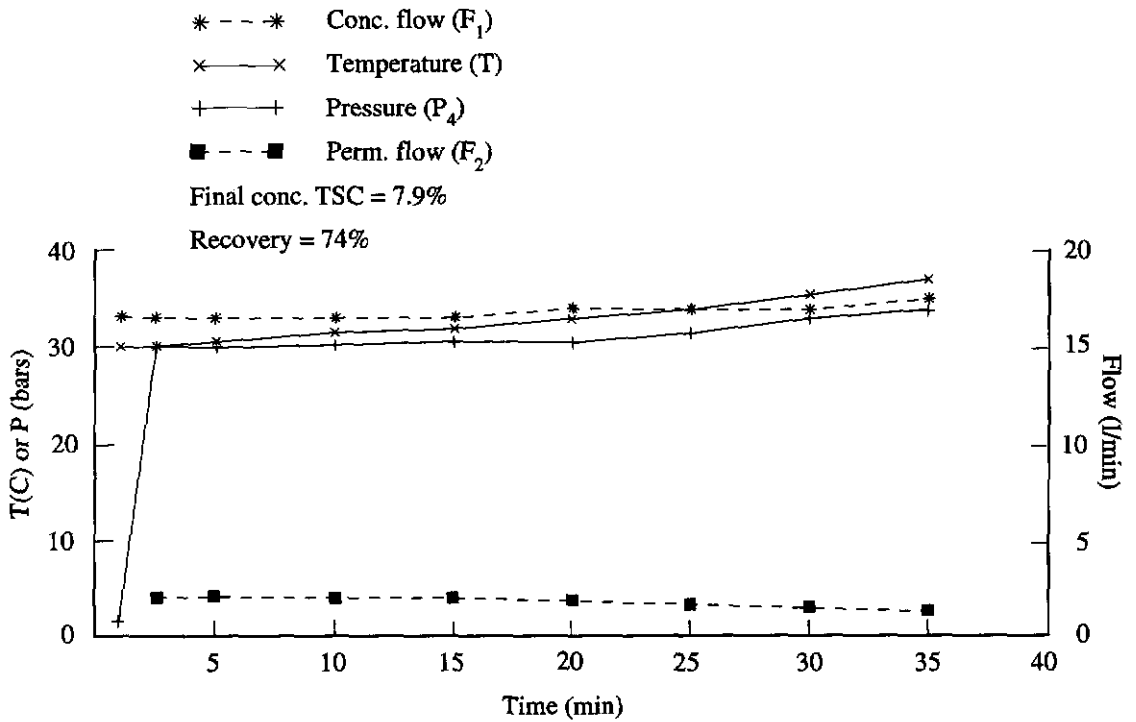


Figure 7. RO using diluted NRSC (Initial TSC = 3.2%)

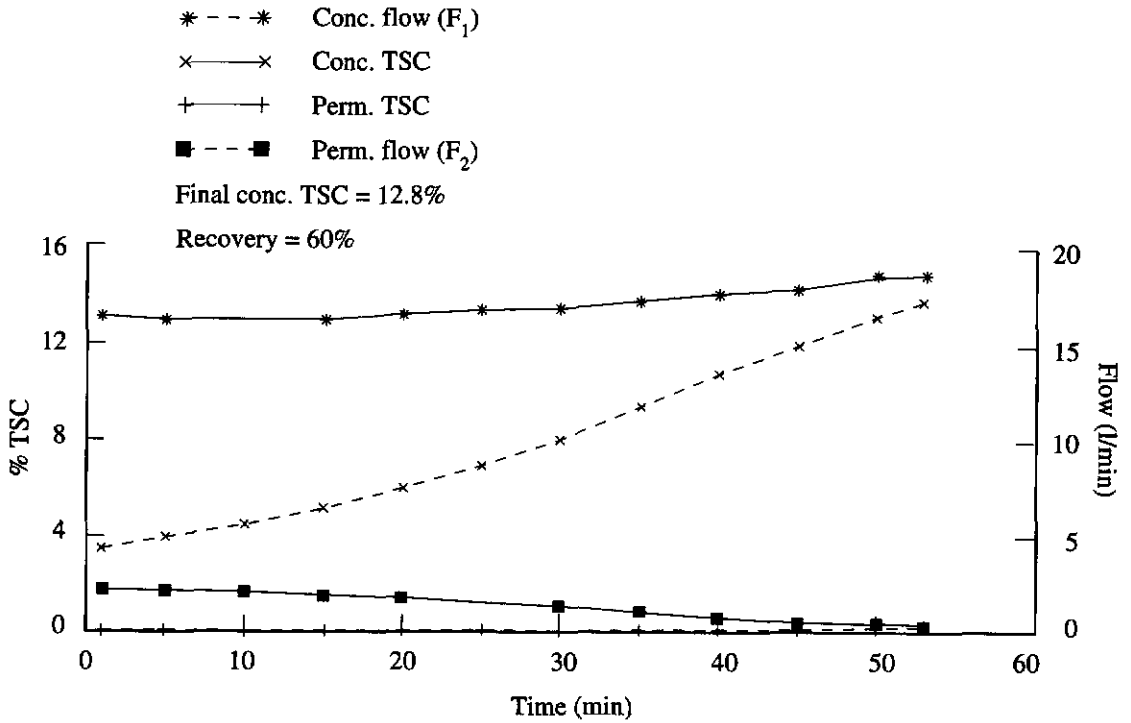


Figure 8. RO using diluted NRSC (Initial TSC = 3.4%)

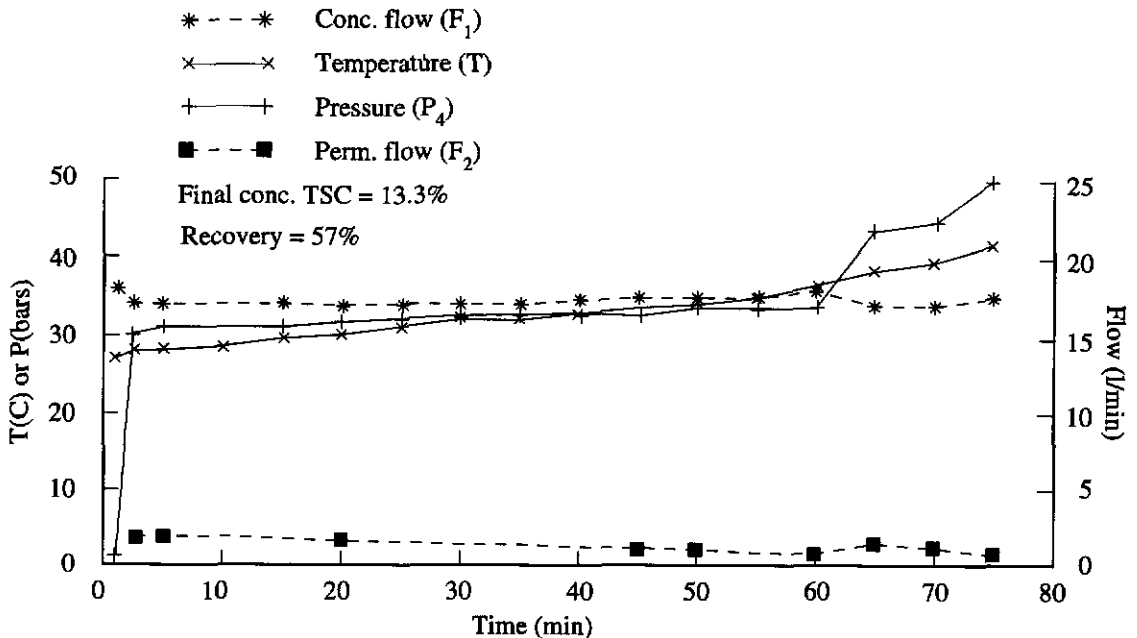


Figure 9. RO using skim NRS (Initial TSC = 3.9%)

for the NaCl solutions for the same concentrations used. *Figure 7* shows a typical chart of the various parameters monitored during the course of the run. The final concentration factor and % recovery of material from the run were quite good and comparable to those of the NaCl runs. *Figure 8* shows the change in the TSC of the concentrate and the permeate, as well as the changes in their flow rates with running time. The rise in concentrate TSC with time was noted to be slightly S-shaped which suggest that the maximum rate of this increase occurred about midway at its inflexion point.

RO Runs using Skim NRS

Due to the milky nature of the skim NRS, it was necessary to store it overnight and then pre-filter it before use. The serum was used at its incoming TSC (without dilution) of between 3.5 and 4.5% (w/w). Typical plots of the parameters recorded against running time are shown in *Figures 9, 10* and *11*. In *Figure 9*, the run was made using an initial pressure (P_1) of 30 bars, which was then raised to 40 bars and finally to 50 bars, after 60 min of running, in order to raise the permeate flow. *Figure 10* on the other hand, showed a run where the initial pressure (P_1) used was 40 bar, and hence the initial permeate flow was higher and a reasonable flow could still be obtained after 45 min of running; however, the temperature rose much quicker and exceeded the safety limit of 45°C after 45 min, which consequently caused the RO unit to stop. *Figure 11* shows the gradual rise in the TSCs of the concentrate and the permeate, and the changes in their flow rates for a typical skim NRS run, which were similar to those of *Figure 8*. As similarly observed with the NaCl and diluted NRSC runs, feed sera with low initial TSCs tend to give higher concentration factors but lower % recoveries than those of higher initial TSCs.

RO Runs using SMR (Block Rubber) NRS

Several RO runs were also made with SMR serum which had an average TSC of about 2% (w/w). As in the case of the skim NRS, the SMR serum was left to stand overnight and then pre-filtered before use. A typical record of such a run is shown in *Figure 12*. Due to the low initial TSC of the serum, the concentration factors from such runs tend to be high, but these are obtained at the expense of rather poor recoveries.

Concentration Factor versus Recovery for NRS Runs

The variation of concentration factor with recovery for all the various NRS runs (*viz.* diluted NRSC, skim NRS and SMR NRS) was plotted and found to be an inverse relationship (*Figure 13*), just like the one for NaCl. However, the absolute concentration factor and recovery values for the NRS runs were generally lower, and the slope of the plot was less steep than that of the NaCl one. This could imply that whilst the pressure requirement for concentrating NRS by RO was much less than that for NaCl for equivalent concentration levels, the amounts of concentration and recovery obtainable were less. A possible reason for this could be due to the greater amount of fouling of the membrane caused by the NRS *vis-a-vis* that of NaCl.

Quality of Permeate derived from NRS Runs

Effluent tests such as total solids, suspended solids, COD and BOD were carried out on the permeates derived from the various NRS runs. A comparison of the typical quality of the permeates derived from SMR NRS, Skim NRS and Diluted NRSC is shown in *Table 1* and

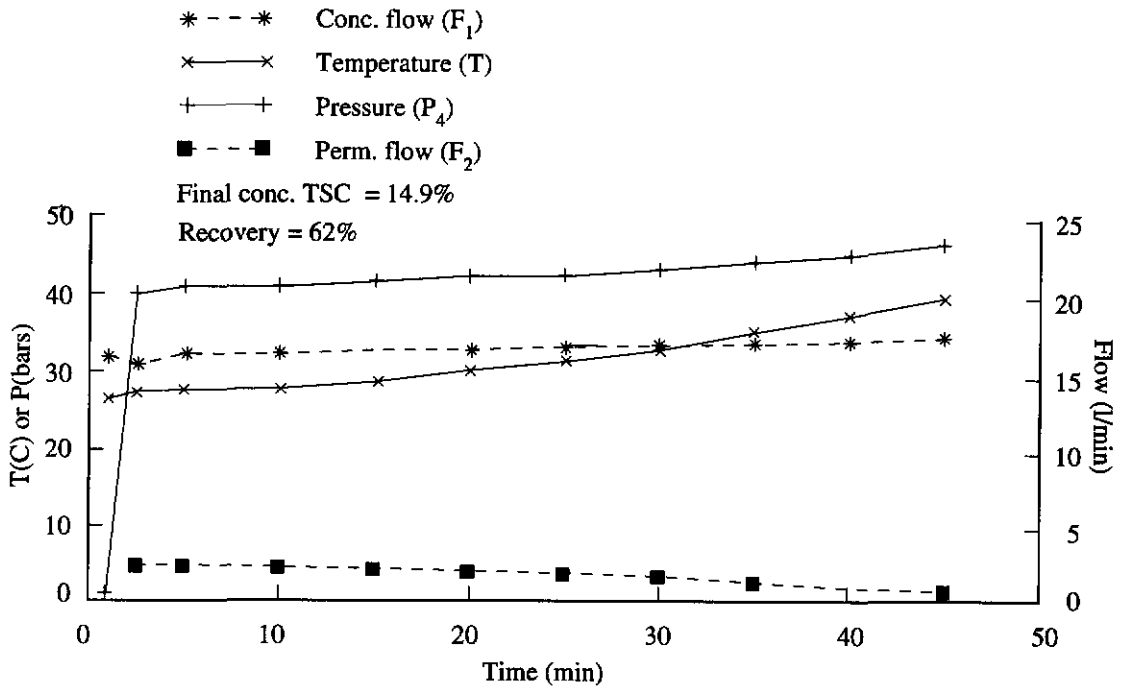


Figure 10. RO using skim NRS (Initial TSC = 4.4%)

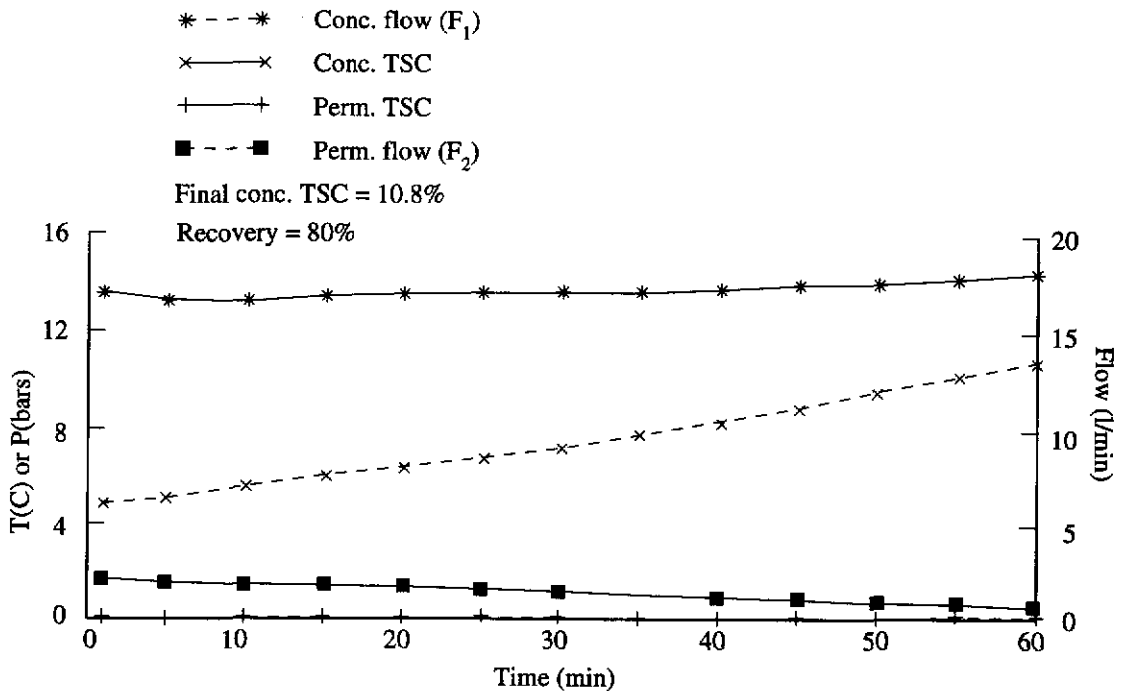


Figure 11. RO using skim NRS (Initial TSC = 4.8%)

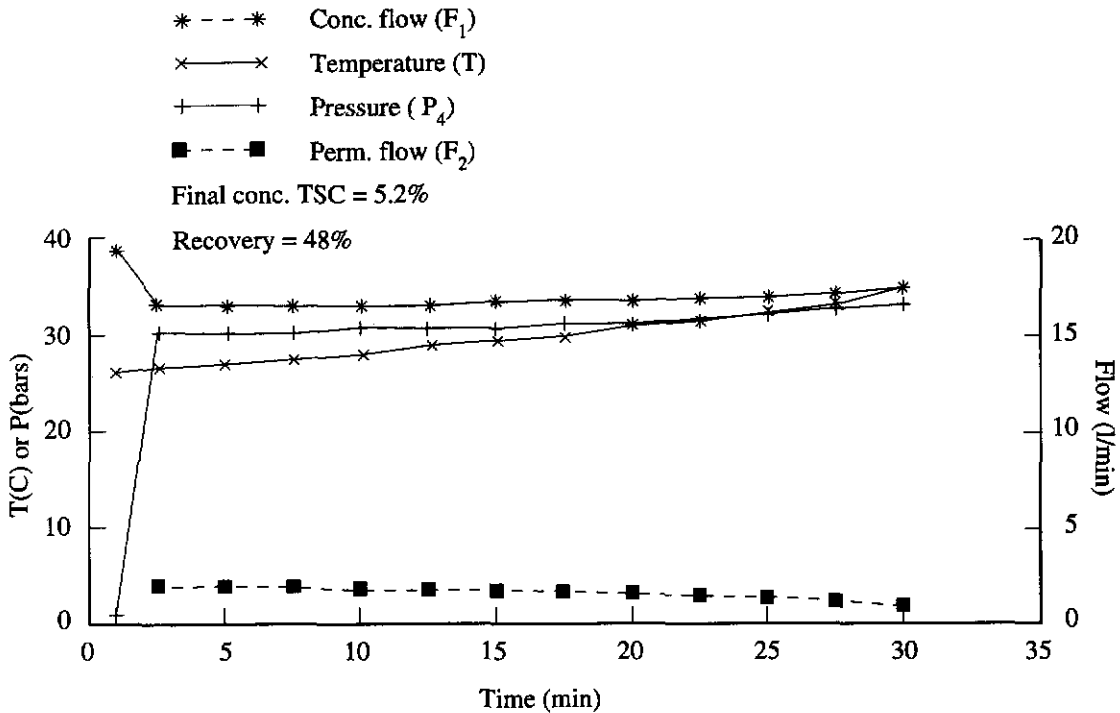


Figure 12. RO using SMR NRS (Initial TSC = 2.0%)

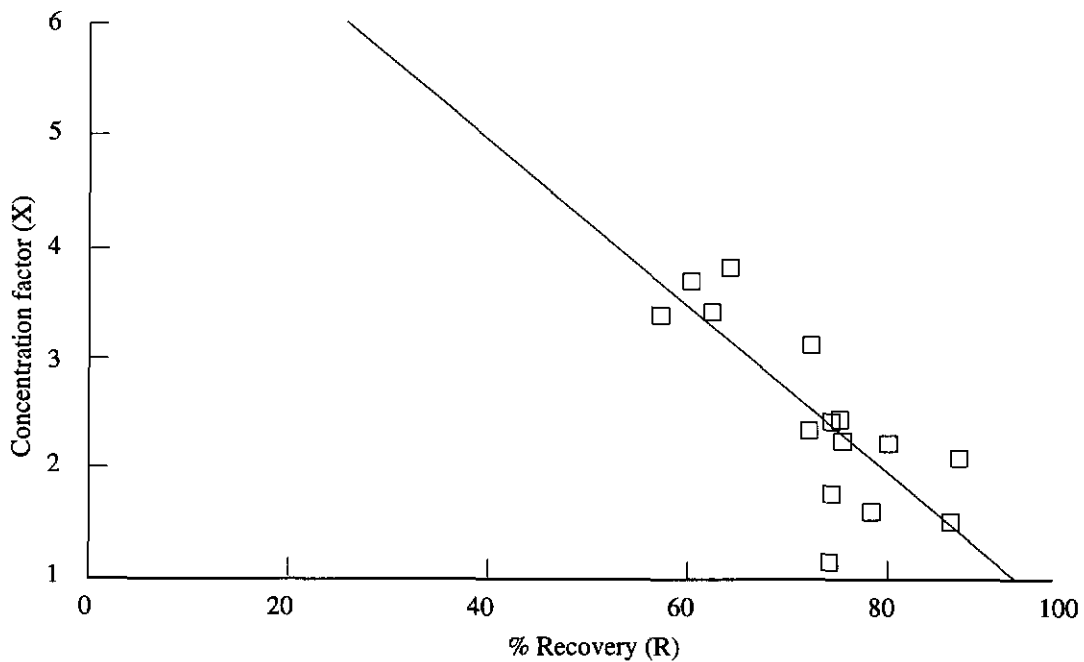


Figure 13. Analysis of RO runs with NRS (Concentration factor versus recovery).

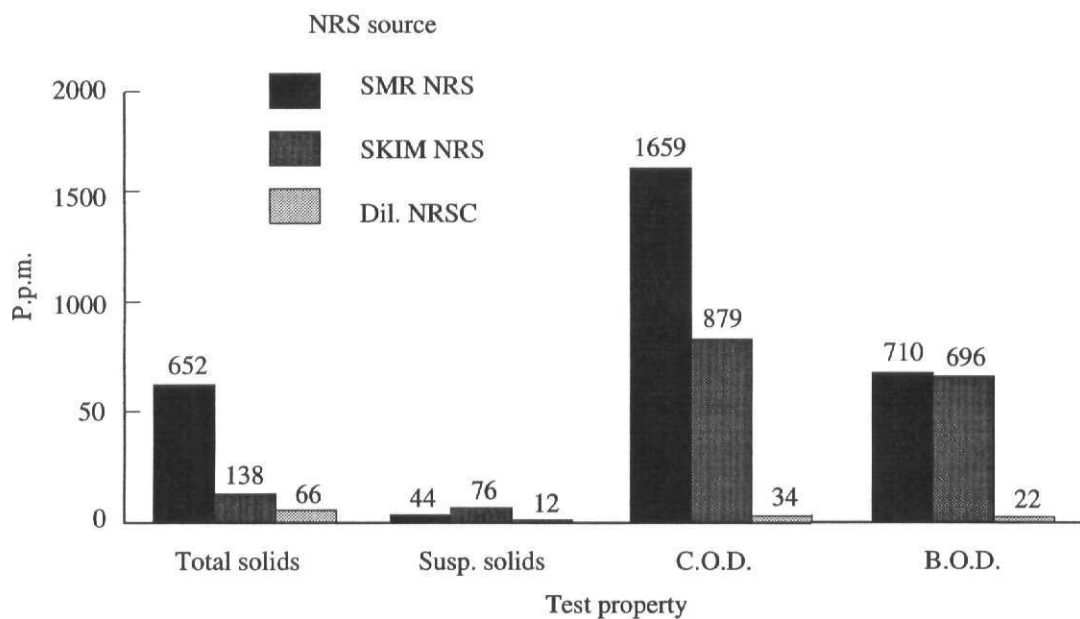


Figure 14. Quality of permeates from different NRS sources.

TABLE 1. QUALITY OF PERMEATES FROM VARIOUS SERA

Permeate type Parameter	SMR serum	Skim serum	Diluted NRSC
Total solids (p.p.m.)	652	138	66
Suspended solids (p.p.m.)	44	76	12
B.O.D. (p.p.m.)	1 659	879	34
C.O.D. (p.p.m.)	710	696	22
pH	2.55	4.0	3.2

P.p.m. = Parts per million

TABLE 2. QUALITY OF PERMEATES FROM MODIFIED SERA

Permeate type Parameter	Skim NRS control	Skim NRS + NaOH	Skim NRS + Ca(OH) ₂	2-week RO-NRSC
Total solids (p.p.m.)	176	178	364	192
Suspended solids (p.p.m.)	20	64	84	64
B.O.D. (p.p.m.)	271	83	118	121
C.O.D. (p.p.m.)	437	224	308	4 738
pH	2.3	9.8	8.75	3.8

P.p.m. = Parts per million

Figure 14. The results show that whilst the total and suspended solids of the various permeates were relatively low, the BOD and COD levels were rather high except for the permeates obtained from NRSC. The low pH values and bad smell of these permeates suggested that the cause of the high BOD and COD values was the presence of volatile fatty acids (VFA), which had permeated through the membrane together with the water because of their small molecular size. The permeates from the NRSC on the other hand, did not have such high BOD and COD values because most of these VFA would have vaporised off during the production of the NRSC by the evaporation process.

Attempts at improving the permeate were made by neutralising the feed NRS (to pH 7) using sodium hydroxide or calcium hydroxide before passing through the ROM. Neutralisation using sodium hydroxide did not improve the permeate quality but raised its pH to a high value of 8.9, obviously because the hydroxide ions had permeated through the membrane (*Table 2*). The use of calcium hydroxide was thought to precipitate the sulphate ions present in the skim NRS besides neutralising the serum. The results showed that the excess hydroxide ions had permeated through the membrane as evident by the high pH, and again, there was no improvement in the permeate quality.

The results in the last column of *Table 2* show the quality of the permeate obtained from a RO run using the combined concentrates from two earlier runs but diluted beforehand. This permeate had a very high COD, presumably because of the fermented nature of the feed which was about two weeks old. This was not surprising because unlike the evaporation process where high temperature heating was involved, bacteria in the serum were not killed during the RO process. In fact, due to the more concentrated nutrients present,

fermentation took place even more rapidly, particularly under hot weather conditions, leading to greater production of VFAs.

Fouling of the membrane was observed to occur after each run with NRS, and was evidently the main reason for its decreasing performance with running time. The module's performance was however, easily restored by cleaning it with a 0.5% solution of sodium hydroxide followed by rinsing with deionised water after each run. Most runs were also made so as not to exceed an hour to avoid permanent damage to the membrane. Thus, it would appear that the type of membrane currently used in the ROM was not selective enough to give a good quality permeate.

CONCLUSION

The above studies show that reverse osmosis can at best, concentrate NRS to concentrations of about 12% (w/w) compared to concentrations of over 60% (w/w) obtainable by the evaporation technique. Therefore, RO on its own cannot be used to overcome the problem of pollution from natural rubber producing factories. However, it can be used as a complement to the established evaporation process; namely for pre-concentrating the dilute NRS derived from both block rubber production as well as from latex concentrate production before further concentration of the serum using the evaporation process. Such a step would be desirable to save energy costs since it is well-known that the energy required for the evaporation process increases exponentially with increasing amounts of water to be removed from feed-solutions of low TSCs, whereas in the RO process, the energy requirement is the opposite way around, *viz.* low for low TSC feed-stock and high for high TSC feed-stock. Transportation costs for raw serum could also conceivably be reduced if it was pre-concentrated by the RO process at a

producing factory before it was transported to a central processing evaporation plant. However, the actual advantages and benefits of such a process would need to be established and weighed against its capital and operational costs, in particular, the high cost of the membrane which would need to be replaced at periodic intervals. Since the present equipment used was only a pilot plant and could not be tested continuously over a long period of time, a full evaluation and costing of the envisaged commercial process could not be made.

Results of studies to-date on the pilot plant RO unit supplied by YRC show that concentration factors of up to 3.8 and recoveries of up to 87% can be obtained from runs with NRS, but both high values cannot be obtained at the same time. The observations instead confirm theoretical prediction of an inverse relationship between concentration factor and recovery.

The poor quality of the resulting permeates from the NRS runs suggest that the aromatic polyamide membrane currently tested in the RO module may not be suitable for use with NRS. It would therefore be of interest to examine the use of other types of membranes on NRS.

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REFERENCES

1. LAU, C.M., SUBRAMANIAM, A. AND TAJIMA, Y. (1989) Recovery and Applications of Waste Solids from Natural Rubber Serum. *Proc. Rubb. Growers' Conf. Malacca 1989*, 525.
2. MYFEC (1990) Mardec-Yokohama Fertilizer Corporation Sdn. Bhd. Company Brochure.
3. LAU, C.M., TAJIMA, Y. AND MACHIDA, M. (1989) Natural Rubber Serum Concentrate and Method for making the Same. *Malaysian Pat. Applic. PI 8901670*.
4. KIRK-OTHMER (eds.) Reverse Osmosis, *Encyclopedia of Chemical Technology*, 3rd edition, Vol. 20, 230.
5. CROLL, B.T. (1992) Membrane Technology: The Way Forward? *J. Instn for Wat. & Environ. Management*, 6(2), 121.
6. LAU, C.M. (1992) Osmotic Pressure Determinations. *Applied Chemistry & Processing Division Internal Report No. 24, RRIM*.
7. ZAID ISA, YONG, W.M. AND SINGH, M.M. (1979) *Laboratory Methods for Chemical Analysis of Rubber Effluents*. Kuala Lumpur: Rubber Research Institute of Malaysia.