EVALUATION OF MEMBRANE TECHNOLOGY FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

Final Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

The salinity levels of tannery effluents discharged into the municipal water treatment system are high (conductivities of 1 500 to 2 000 mS/m) and unacceptable to municipal authorities because it increases the mineralization of the country's limited water resources. Final effluent discharges into municipal water treatment systems should have a conductivity of less than 500 mS/m to render the effluent suitable for discharge into the system. Hence, there is a need to desalinate tannery effluent effectively, prior to discharge into municipal water treatment systems.

The concentration levels of organic materials and ammonia-nitrogen in tannery effluents are also high. Concentration levels of organic matter and ammonia-nitrogen of 2 000 to 3 000 mg/ℓ Chemical Oxygen Demand (COD) and 450 mg/ℓ have been reported, respectively. COD and ammonia-nitrogen concentration levels of <3 000 mg/ℓ COD and 40 to 50 mg/ℓ ammonia-nitrogen, respectively, are regarded as being acceptable discharge concentration levels to municipal water treatment systems. Consequently, it is also neccesary to remove excess COD and ammonia-nitrogen from tannery effluents, prior to discharge into the municipal treatment system.

Sulphide and chromium concentration levels in tannery effluents should be less than 40 and 5 mg/ℓ, respectively, prior to discharge. Sulphide and chromium concentration levels may exceed these limits in certain cases and have to be removed from the effluent, prior to discharge into the municipal treatment system.

Tannery effluent consists of various streams contributing different salinity, organic and ammonia-nitrogen concentration levels to the final combined effluent. Tannery effluent consists of soak paddle effluent, liming effluent, deliming effluent, tanning effluent and dye-house effluent. The soak paddle and certain parts of the tanning effluent (pickle tan and chrome work) are the major contributors to the salinity level of the final effluent.

It may be possible to reduce the contaminant level in tannery effluent to acceptable discharge concentration levels with reverse osmosis (RO) technology. Tannery effluents, however, have a high fouling potential for RO membranes due to the high organic and inorganic concentration levels of the effluents. Little information is available in the literature regarding pretreatment methods for tannery effluent, prior to RO desalination. Ultrafiltration (UF) and/or microfiltration (MF) may be suitable technologies to protect RO membranes from fouling during treatment of tannery effluent. Little information is also available regarding membrane cleaning procedures and process performance as a function of time.

Almost no information could be found in the literature regarding treatment of segregated streams in a tannery with membrane technology. Most of the individual streams are highly contaminated with organic matter, with the result that these streams have a high potential to foul membrane systems. However, the combined final effluent is pretreated with coagulants and dissolved air

flotation prior to discharge into the municipal treatment system. Consequently, this pretreated, combined final effluent should theoretically have a lower fouling potential for membrane systems. It was, therefore, decided to first evaluate the desalination of the final combined effluent before attempting to desalinate individual streams in a tannery.

The objectives of the study were to evaluate:

- UFRO treatment of the pretreated, combined final effluent;
- MFRO treatment of the soak paddle effluent;
- UFRO treatment of the dye-house effluent;
- UFRO treatment of the liming effluent;
- UFRO treatment of the deliming effluent.

The combined final effluent produced by Hanni Leathers, despite pretreatment in a Silflo unit, rapidly fouled polysulphone UF membranes. Ultrafiltration permeate flux levels soon dropped to low levels. Permeate flux varied between approximately 100 and 400 ℓ/m^2.d. However, it may be possible to control membrane fouling by pH adjustment of the effluent and regular cleaning of the membranes with a warm water rinse, followed by cleaning with an enzymatic cleaning and oxidising agent.

The COD of the UF feed varied between 1 500 and 4 000 mg/ℓ over the test period. However, poor COD removals were obtained. COD removals varied between 6 and 32 percent. This showed that most of the organic materials in the effluent had a relatively low molecular masses (40 000 molecular mass cut-off UF membranes were used).

Chromium, iron, sulphate, fats and oils were removed with UF treatment of the effluent. These chemicals are all potential membrane fouling agents which could have contributed to UF membrane fouling. However, no membrane foulants were removed from the surface of the membranes for analytical identification. Further work should be done to identify these foulants analytically.

Membrane fouling was experienced when the final effluent was treated with UFRO (polysulphone UF and PCI AFC 99 nanofiltration RO membranes). Low permeate fluxes were experienced. Ultrafiltration and RO permeate fluxes of approximately 150 to 500 ℓ/m^2.d and 100 to 150 ℓ/m^2.d, respectively, were experienced. Fouling of the RO membranes occurred despite the use of ultrafiltered water as feed to the RO membranes. It was noticed that the UF permeate became milky on standing. This could be ascribed to coagulation/flocculation of proteins in the effluent. This material may have contributed to the membrane fouling encountered and these substances should be analysed.

The electrical conductivity of the effluent was not significantly reduced by the nanofiltration RO membranes. The electrical conductivity of the feed solution varied between approximately 600 and 2 500 mS/m. The electrical conductivity of the RO permeate varied between approximately 500 and 1 500 mS/m. Hence, the electrical conductivity remained high, and reductions varied between approximately 29 and 37 percent. These low reductions may be ascribed to the high percentage of monovalent ions, compared to the divalent ions, in the RO feed.

Good COD removals were obtained with the nanofiltration RO membranes. The COD of the RO feed varied between 1 250 and 2 300 mg/ℓ. Permeate COD varied between 600 and 900 mg/ℓ. Hence, COD removals of between 20 and 66 percent were attainable.

Membrane fouling was also experienced during UFRO treatment of the final effluent when polysulphone UF (80% recovery) and cellulose acetate RO (70% recovery) membranes were used. The UF permeate flux was low (approximately 250 ℓ/m^2.d). It was possible to control UF membrane fouling with regular chemical cleaning. Relatively low permeate fluxes were experienced during RO treatment of the UF permeate. Permeate flux varied between 110 and 350 ℓ/m^2.d. Membrane fouling was also experienced despite the UF permeate that was used as feed to the RO unit. Reverse osmosis brine comprises approximately 30 percent of the RO feed. This brine contains high consentrations of inorganic materials and should rather be disposed of than be used as part of the RO feed solution.

The COD of the RO feed (UF permeate) varied between 2 500 and 5 160 mg/ℓ. The COD of the RO permeate varied between 500 and 1 090 mg/ℓ during the test run. COD removals varied between 72 and 90 percent. Hence, good COD removals were obtained with RO. However, a significant amount of low molecular mass organics was retained in the permeate.

Good turbidity and COD removals were obtained with alum coagulation/flocculation of the soak paddle effluent. Turbidity could be reduced from 1 750 to 60 NTU (96,0% removal) at an Al^{3+} dosage of 150 mg/ℓ. COD was also reduced from 12 000 to 3 400 mg/ℓ (71,7% removal).

Excellent turbidity removal was obtained from the soak paddle effluent with CFMF (polyester membranes). In one instance turbidity was reduced from 1 700 NTU in the feed to 3,5 NTU in the permeate. COD was reduced from 12 000 mg/ℓ in the feed to 6 730 mg/ℓ in the permeate (43,9% removal).

RO treatment yielded poor results with a concentrated soak paddle effluent. Electrical conductivity was reduced from 7 160 to 3 830 mS/m (46,5% reduction) at a water recovery of approximately 70 percent. COD was removed from 2 790 to 890 mg/ℓ (68,1% removal). The average permeate flux during a batch RO run was 75,5 ℓ/m^2.d. This low flux could be ascribed to membrane fouling and the high osmotic pressure of the feed. The electrical conductivity and COD of the brine were high, 10 780 mS/m and 5 830 mg/ℓ, respectively.

Improved results were obtained during RO treatment of a more dilute soak paddle effluent. Feed electrical conductivity was reduced from 2 700 to 509 mS/m in one case (81,1% removal, water recovery approximately 80%). The average permeate flux was 200 ℓ/m^2.d. Ammonia-nitrogen was reduced from 77,98 to 21,8 mg/ℓ (72,8% removal). COD was reduced from 1 070 to 125 mg/ℓ (88,3% removal). Brine volume comprised 20 percent of the treated volume. The electrical conductivity of the brine was 7 010 mS/m in this case and the ammonia-nitrogen concentration was 165 mg/ℓ. The fluoride, sodium and chloride concentration levels were 9,9; 13 630; and 21 225 mg/ℓ, respectively.

Good results were obtained with treatment of the sump effluent (effluent from soak paddles, fleshing, splitting, deliming) with RO. Electrical conductivity was reduced from 1 104 to 128 mS/m (88,4% reduction). COD was reduced from 3 720 to 90 mg/ℓ (97,5% removal). The average permeate flux was 330,5 ℓ/m^2.d. It may be possible to control membrane fouling with regular chemical cleaning. The electrical conductivity (3 620 mS/m) and COD (4 330 mg/ℓ) of the brine were high. The brine comprised 12,5 percent of the treated water.

Membrane fouling was experienced during treatment of the dye-house effluent with UF, but this may be controlled by regular chemical cleaning. Permeate flux was low (approximately 144 ℓ/m^2.d). Water recovery was 90 percent. A COD removal of 67,5 percent was obtained (reduced from 22 900 to 7 440 mg/ℓ). The brine (10% of feed volume) contained 79 000 mg/ℓ COD and the electrical conductivity was 1 307 mS/m.

Membrane fouling was also experienced during RO treatment of the UF permeate. The average permeate flux was 272 ℓ/m^2.d during a batch run. Water recovery was 80 percent. The feed electrical conductivity was reduced from 1 181 mS/m to 156 mS/m (86,8% reduction). Ammonia-nitrogen and COD were removed from 456,1 to 64,2 mg/ℓ (85,9% removal) and 6 710 to 963 mg/ℓ (85,7% removal), respectively. The electrical conductivity (3 480 mS/m) and ammonia-nitrogen (1 494 mg/ℓ) concentration levels in the brine were high. The chromium (vi) concentration level in the brine was also high (2,0 mg/ℓ).

Membrane fouling was experienced during the treatment of the liming effluent with UF. Permeate flux was low (approximately 290 ℓ/m^2.d). Water recovery was approximately 90 percent. A COD removal of 82,7 percent was obtained (reduced from 21 650 mg/ℓ in UF feed to 3 750 mg/ℓ in UF permeate). The electrical conductivity of the UF brine (1 167 mS/m) as well as the COD were high (67 600 mg/ℓ). The chromium (vi) concentration level of the brine was also high (0,2 mg/ℓ).

Preliminary work showed that little, if any, membrane fouling occurred during treatment of the ultrafiltered liming effluent with RO. The average permeate flux was 687,5 ℓ/m^2.d and water recovery was 82 percent. The electrical conductivity of the RO feed was reduced from 654 to 154 mS/m (76,5% removal). COD was removed from 3 100 mg/ℓ in the RO feed to 280 mg/ℓ in the RO permeate (90,97% removal). The electrical conductivity (1 963 mS/m) and the COD (8 800 mg/ℓ) of the brine were high.

Membrane fouling was experienced when the deliming effluent was treated with UF. Permeate flux was low (approximately 264 ℓ/m^2.d). It was not possible to restore the flux completely after chemical cleaning as was the case with the liming effluent. Further work will be required to evaluate alternative membrane cleaning methods. Water recovery was approximately 90 percent. The COD of the effluent was reduced from 16 500 to 3 580 mg/ℓ (78,3% removal). The electrical conductivity (1 700 mS/m) and the chromium (iv) (2,0 mg/ℓ) concentration level of the deliming effluent were high.

Preliminary work has shown that almost no membrane fouling took place during treatment of the deliming effluent with RO. The permeate flux (average flux) was determined at 467 ℓ/m^2.d.

Water recovery was approximately 80 percent. The electrical conductivity of the RO feed was reduced from 1 017 mS/m to 349 mS/m (65,7% removal) and the COD from 3 350 to 620 mg/ℓ (81,5% removal). The electrical conductivity (1 552 mS/m) and COD (9 200 mg/ℓ) of the RO brine were high.

In all the above cases, where individual effluent streams were treated, it is imperative that the brines be disposed of in a satisfactory manner.

In summary, all contract objectives have been achieved in this study. It was shown that:

- UFRO may be used for treatment of the combined pretreated final effluent;
- MFRO could be used for treatment of the soak paddle effluent; and
- UFRO for treatment of the dye-house effluent, liming effluent, and deliming effluent.

This report offers the following to potential users of membrane technology in the treatment of tannery effluents:

- It presents process design criteria for the treatment of tannery effluent streams with membrane technology;
- It identifies suitable membrane processes that may be used for soak paddle effluent, dye-house effluent and liming and deliming effluents.

The following actions will be taken as a result of the study:

- Results of the investigation will be published in *Water SA* and presented at a local conference;
- A seminar on the treatment of tannery effluents with membrane technology will be presented to the tannery authorities in South Africa.

The following recommendations may be made as a result of the study:

- The overall economics of treatment of tannery effluents with membrane technology should be determined;

- Ceramic MF/UF membranes should be evaluated for treatment of tannery effluent prior to RO desalination;

- Physical/chemical technologies (flotation; filtration; coagulation/flocculation) should be fully evaluated for pretreatment of tannery effluents prior to RO desalination;

- Evaporation technologies should be evaluated for treatment of the RO brine to effect zero effluent discharge from a tannery.

1. INTRODUCTION

The salinity discharge level of tannery effluents into the municipal water treatment system is high (1 500 to 2 000 mS/m) and not acceptable to the municipal authorities because it causes mineralization of the nations limited water resources[1]. Final effluent discharges into the municipal water treatment system should contain less than 500 mS/m salinity to make the effluent fit for discharge into the system. Consequently, a need exists to desalinate tannery effluent effectively prior to discharge into the municipal water treatment system[1].

The organic and ammonia-nitrogen concentration levels in tannery effluents discharged into the municipal treatment system are also high. Organic and ammonia-nitrogen concentration levels of 2 000 to 3 000 mg/ℓ COD and 450 mg/ℓ have been reported, respectively. Chemical oxygen demand and ammonia-nitrogen concentration levels of <3 000 mg/ℓ COD and 40 to 50 mg/ℓ ammonia-nitrogen, respectively, are acceptable discharge concentration levels to the municipal water treatment system. Consequently, a need also exists to remove excess COD and ammonia-nitrogen from tannery effluents prior to discharge into the municipal treatment system.

Sulphide and chromium concentration levels in tannery effluents should be less than 50 and 5 mg/ℓ, respectively, prior to discharge. Sulphide and chromium concentration levels may exceed these limits in certain cases and needs to be removed from the effluent prior to discharge into the municipal treatment system.

Tannery effluent consists of various streams contributing different salinity, organic and ammonia-nitrogen concentration levels to the final combined effluent. Tannery effluent consists of soak paddle effluent, liming effluent, deliming effluent, tanning effluent and dye-house effluent. The soak paddle and certain parts of the tanning effluent (pickle tan and chrome work) contribute most to the salinity level of the final effluent.

It should be possible to reduce the contaminant level in tannery effluent to acceptable discharge concentration levels with reverse osmosis (RO) technology. Tannery effluents, however, have a high fouling potential for RO membranes due to the high organic and inorganic concentration levels of the effluents[2]. Little information is available in the literature regarding pretreatment methods for tannery effluent prior to RO desalination. Ultrafiltration (UF) and/or microfiltration (MF) may be suitable technologies to protect RO membranes from fouling during treatment of tannery effluent. However, very little information is available in the literature in this regard. Little information is also available regarding membrane cleaning procedures and process performance as a function of time. Almost no information could be found in the literature regarding treatment of segregated streams in a tannery with membrane technology[3,4]. Most of the individual streams are highly contaminated with organics with the result that these streams have a high potential to foul membrane systems. However, the combined final effluent is pretreated with coagulants and dissolved air flotation prior to discharge into the municipal treatment system. Consequently, the combined final effluent should have a lower fouling potential for membrane systems. It was therefore decided to first evaluate the desalination of the final combined effluent before attempting to desalinate some of the individual streams in a tannery.

The objectives of the study were therefore to : -

(a) Evaluate UFRO treatment of the combined final effluent;
(b) Evaluate MFRO treatment of the soak paddle effluent;
(c) Evaluate UFRO treatment of the dye-house effluent;
(d) Evaluate UFRO treatment of the liming effluent;
(e) Evaluate UFRO treatment of the deliming effluent.

2. WASTEWATER DRAINAGE AND COLLECTION SYSTEM

Processes conducted at a tannery to prepare leather suitable for consumer products are shown in Figure 1[5]. Wastewater drainage and collection systems are shown in Figures 2 and 3[5]. The tannery is divided in two main sections, namely the Wet-blue and Dye-house sections.

Operations in the Wet-blue section include soaking, pre-wash, unhairing, lime-wash, flushing, washing, delime, bate, tan and tan wash processes[5]. The liquors discharged from the various processes differ in chemical and physical properties as well as volume[5]. Soaking is carried out in paddles while the remaining processes are carried out in drums.

The dye-house discharges its liquors which include retan dyeing and finishing liquors, into a common drain which gravitates to a sump from where they are pumped to the mixing and aeration tank via a rotary screen. Effluent from the operation tank is treated in Silflo units (ferric chloride, polyelectrolyte, dissolved air flotation) prior to discharge into the municipal treatment system. The chemical composition of the exhaust liquors of a tannery is shown in Table 1[5].

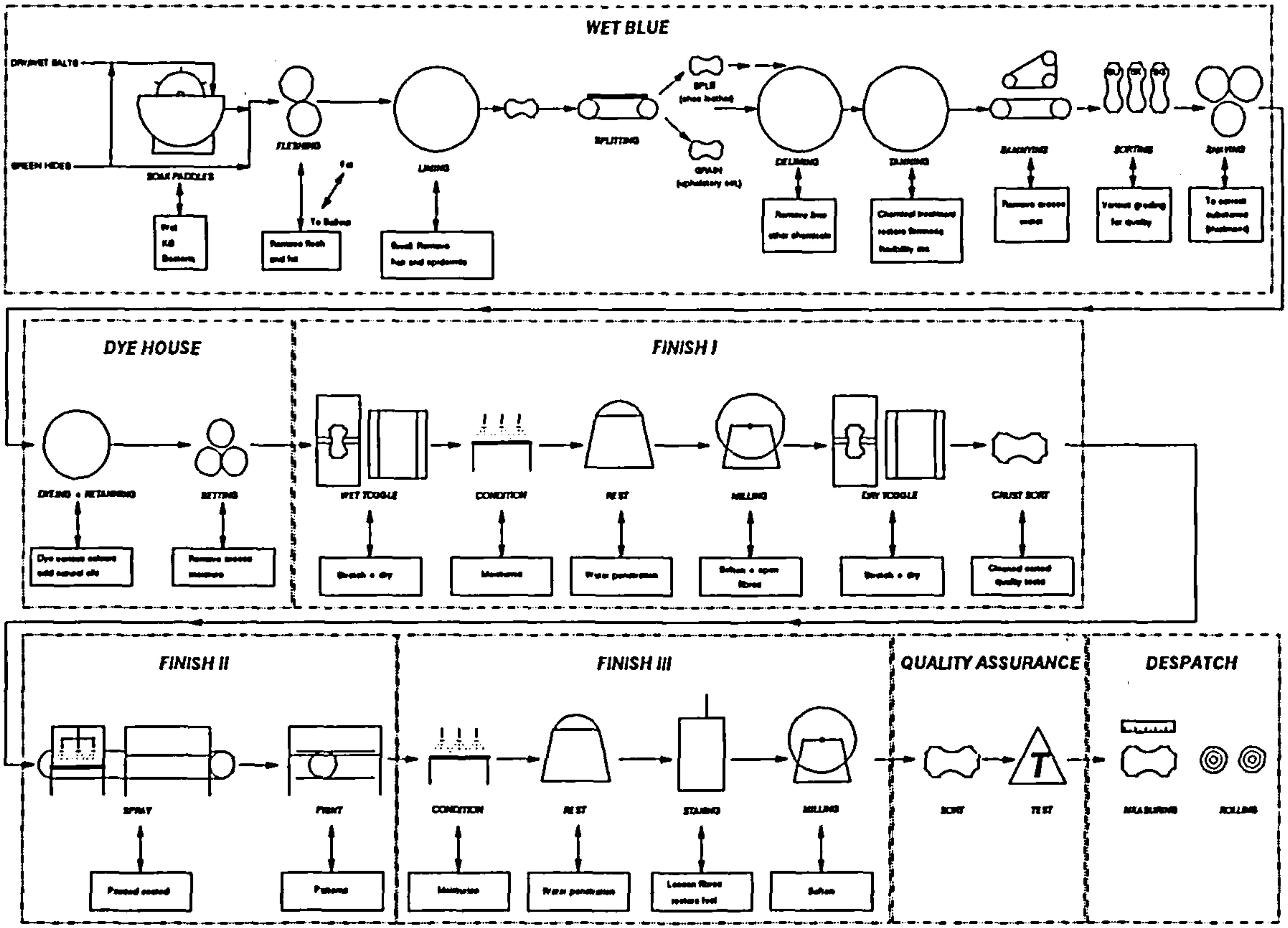

Figure 1 : Schematic presentation of leather tannery process.

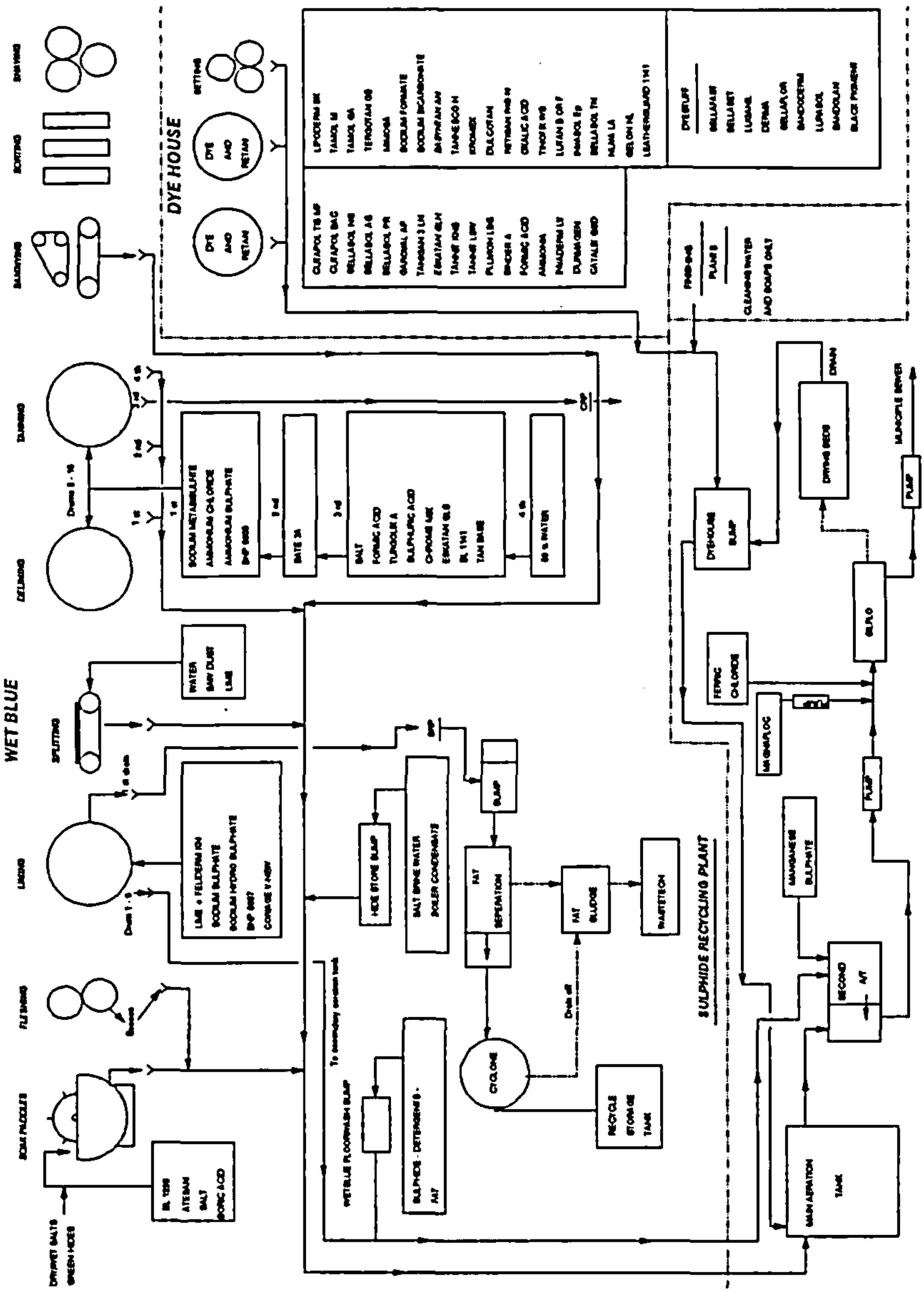

Figure 2 : Schematic presentation of tannery wastewater treatment facility.

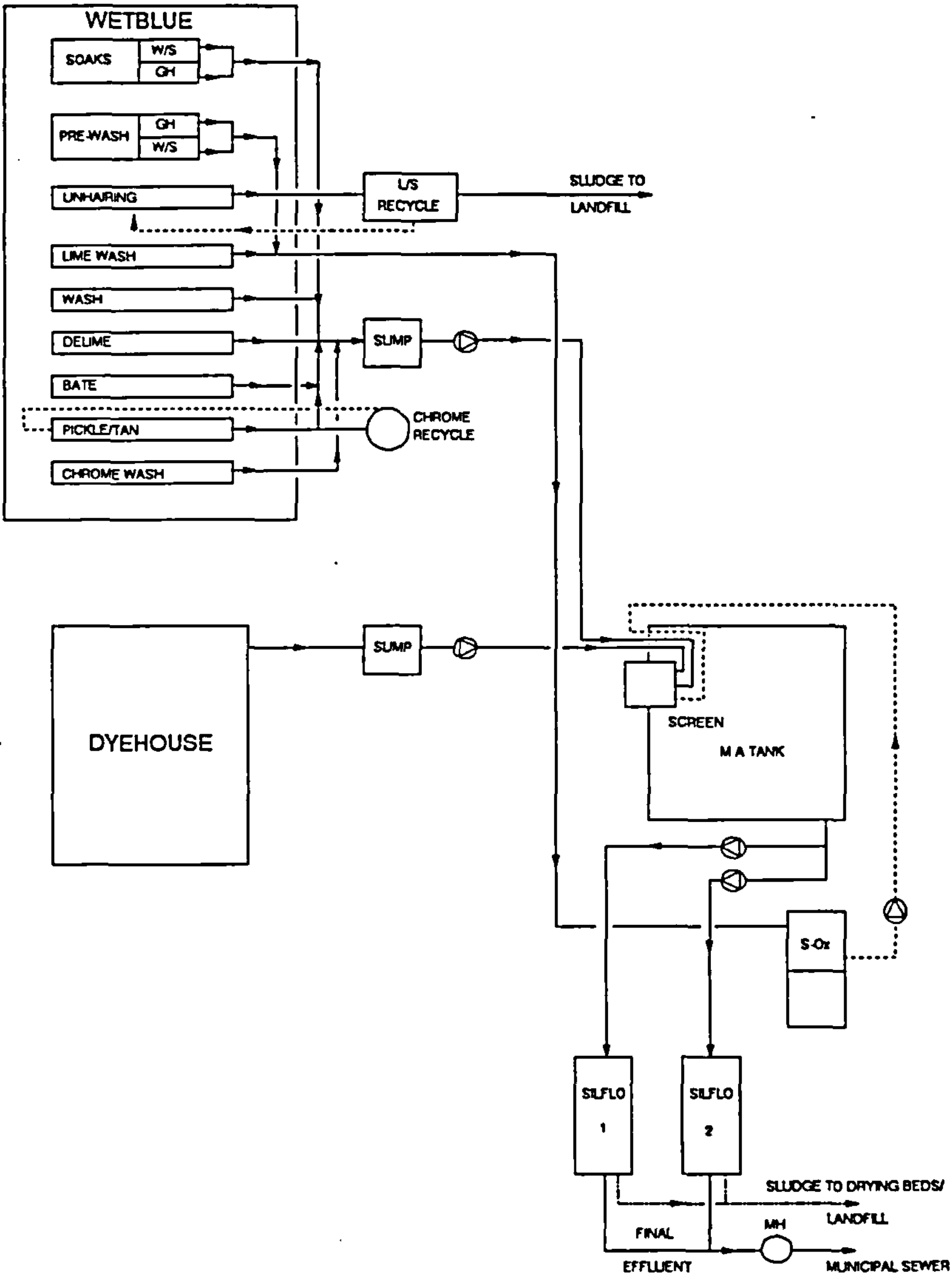

Figure 3 : Simplified diagram of wastewater treatment facility.

Table 1 : Chemical composition of exhaust liquors from a tannery.

Determination	Expressed as	Soak		Pre-lime Wash			Lime Wash	Wash	Delime	Bate	Pickle/ Tan	Chrome Wash	Dye-House	M/A Tank Effluent	Final Effluent
		Green Hide	W/S Hide	W/S-GH Mix	W/S	G/H									
pH		8,8	7,6	7,2	6,8	7.0					4,4	4,5	4,5	7,5	6,2
Conductivity	mS/m	376	4620	842	1490	172					7455	4940	809	1850	1860
COD	mg/ℓ	5420	3540	893	1156	783					N/D	N/D	7140	5324	1133
PV	mg/ℓ	756	476	74	265	179					N/D	N/D	1398	1194	367
SS	mg/ℓ	1462	2496	362	294	336					2384	1449	618	5664	300
TKN	mg/ℓ	470	356	185	188	171					N/D	N/D	641	969	556
NH_3-N	mg/ℓ	225	188	62	37	50					N/D	N/D	470	567	450
ALK - Bicarbonate	mg/ℓ	1260	700	330	260	340					N/D	N/D	380	1080	280
Carbonate	mg/ℓ	100	80	0	0	40					N/D	N/D	0	120	40
Na	mg/ℓ	720	14200	780	1890	295					17050	11750	1550	2010	2120
CL	mg/ℓ	567	11347	603	4610	325					27480	15955	2840	3190	5140
SO_4	mg/ℓ	433	9021	232	766	210					18925	22435	1025	2914	2893
TDIS	mg/ℓ	1140	28580	1550	6430	770					95780	49780	4440	9760	9400
TDS	mg/ℓ	6850	33750	6110	9830	2066					1226615	67590	9800	13540	13070
Sulphide	mg/ℓ	17	5,5	7	4,8	9,5					N/D	N/D		49	30
Chromium	mg/ℓ	N/D	N/D	N/D	N/D	N/D					4530	2330		49	5,4
Boron	mg/ℓ	<1	<1	<1	<1	<1					N/D	N/D	<1	<1	<1
Phosphate	mg/ℓ	<1	<1	<1	<1	<1					N/D	N/D	<1	<1	<1
Iron	mg/ℓ	N/D	N/D												

N/D = Not determined.

3. EXPERIMENTAL

3.1 Ultrafiltration treatment of final effluent

The experimental set-up for the UF studies is shown in Figure 4.

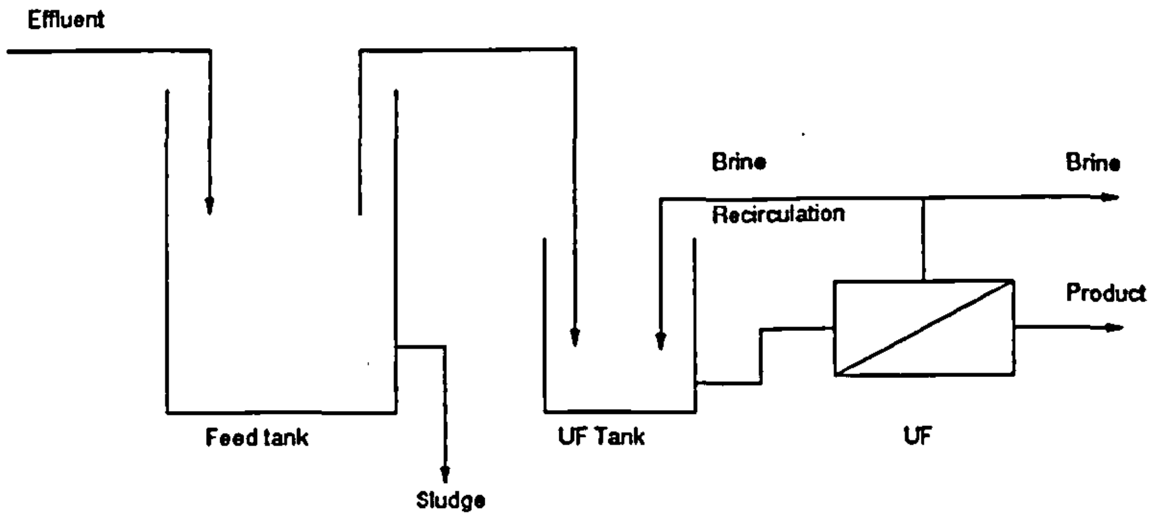

Figure 4 : UF experimental set-up for treatment of final effluent.

Final effluent was pumped into a 1 kilolitre storage tank. Effluent from this tank was pumped into the 500 litre UF feed tank from where it was pumped through two tubular polysulphone UF membrane (12 mm diameter) modules in series (3,5 m^2 and total membrane area). Feed inlet pressures of 200 and 400 kPa were applied. The UF system was provided with a sponge ball cleaning facility with flow reversal. Flow through the membranes was reversed every 20 minutes. Effluent could either be passed once through the system or with brine recirculation to the feed tank. The water level in the UF feed tank was kept constant with a level controller.

3.1.1 *Membrane cleaning*

The following membrane cleaning agents were evaluated during the UF run : -

(a) Tap water;
(b) Warm tap water (approximately 60 °C);
(c) Detergent A (1 to 3%; room temperature and approximately 60 °C);
(d) Sodium hypochlorite solution (approximately 200 mg/ℓ chlorine) adjusted to pH 11 with caustic soda);
(e) Acidic tap water (pH 1,5);
(f) P3 Ultrasil 50 (0,5%); and
(g) EDTA solution (0,5%).

A general procedure for membrane cleaning was as follows : The membranes were rinsed for 20 minutes with tapwater after a UF run and the clean water flux (CWF) of the membranes were then determined. The membranes were then rinsed with cleaning agent for 30 to 60 minutes at reduced pressure. The cleaning agents were circulated through the membranes from a 200 litre container. Steam was used to heat the water to approximately 60 °C where necessary. Sponge ball reversal was applied every 5 minutes during the cleaning cycle. The CWF was determined after every cleaning cycle after the cleaning agent had been properly removed through rinsing from the membranes with tapwater.

3.2 Ultrafiltration reverse osmosis (UFRO) treatment of the final effluent (PCI AFC 30 polyamide membranes)

The experimental set-up for the UFRO studies is shown in Figure 5.

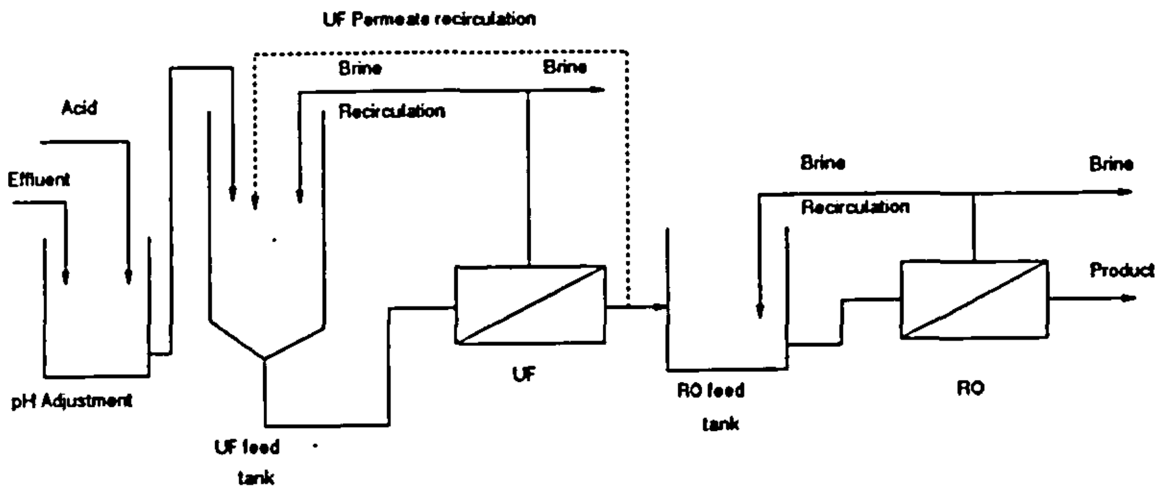

Figure 5 : UFRO experimental set-up for treatment of the final effluent (PCI AFC 30 polyamide nanofiltration membranes)

The pH of final effluent was adjusted to approximately 5 in a one kilolitre tank. Effluent from this tank was passed through four unsupported UF polysulphone membranes (8 m^2 total membrane area). The UF permeate was collected in the RO feed tank from where it was passed through a tubular nanofiltration RO membrane (12 mm diameter) module (PCI AFC 30 polyamide membrane; 1 m^2 membrane area). Both the UF and RO brines were circulated back to the UF and RO feed tanks, respectively. Water recovery was set at approximately 80 percent. The UF and RO units were operated at 200 and 400 kPa, respectively. Samples were taken on a regular basis for COD, conductivity and pH analysis. The chemical composition of the UF and RO feed, brine and permeate was also conducted on a regular basis.

3.3 Ultrafiltration reverse osmosis (UFRO) treatment of the final effluent (cellulose acetate RO membranes)

The experimental set-up for the UFRO studies is shown in Figure 6.

Final effluent was adjusted to a pH of approximately 5 with hydrochloric acid before it was passed through the UF unit (same membrane as in previous case). The UF permeate was collected in a one kilolitre storage tank and pumped into the 200 litre RO feedtank equipped with a level controller. The RO feed was pumped through two tubular cellulose acetate RO membrane (12 mm diameter) modules in series (total membrane area 3,5 m^2). Flow reversal with sponge ball cleaning was applied every 30 minutes.

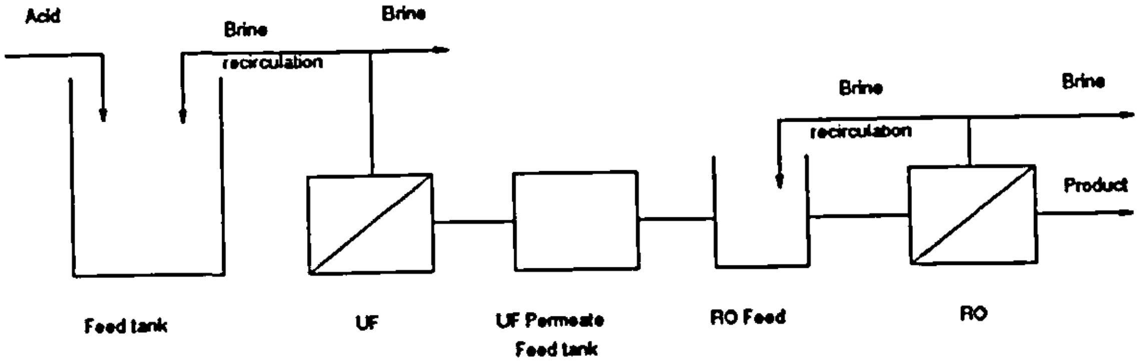

Figure 6 : UFRO experimental set-up for treatment of final effluent (cellulose acetate RO membranes).

Both the UF and RO brines were circulated back to the UF and RO feed tanks. Ultrafiltration and RO water recoveries were set at approximately 80 and 70 percent, respectively. The conductivity, COD and pH of the UF and RO permeates were measured on a regular basis. The chemical composition of the UFRO feed, brine and product was also measured on a regular basis.

3.4 Cross flow microfiltration reverse osmosis (CFMFRO) treatment of soak paddle effluent

The experimental set-up for the CFMF studies is shown in Figure 7.

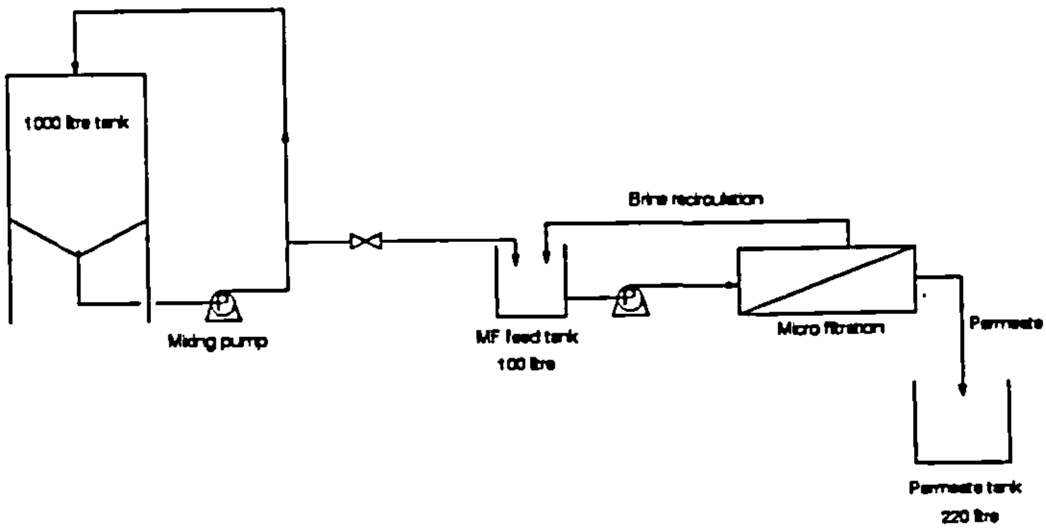

Figure 7 : CFMF experimental set-up for treatment of soak paddle effluent (polyester membranes)

Soak paddle effluent as well as a sample from the sump containing effluent from the soak paddles, fleshing, splitting, deliming and certain stages from the tanning operation were pretreated with CFMF prior to RO desalination (See Fig. 3). The CFMF unit contained woven polyester fabric membranes (12 mm diameter) with a total membrane area of 1,81 m^2. Soak paddle effluent batches with different electrical conductivities and COD concentration levels were treated with CFMFRO. One sample (250 litre) of the sump effluent was also treated with CFMFRO. The initial runs were conducted at a pressure of 200 kPa, but the pressure was reduced to 175 kPa for subsequent runs because feed was leaking into the product water in the manifold system at 200 kPa. The linear flow velocity through the membrane tubes was approximately 4 m/s. The COD of the feed and product, turbidity of the product, temperature of the feed and water recovery were measured on a regular basis.

The RO unit contained two tubular cellulose acetate RO membrane (12 mm diameter) modules with a total membrane area of 3,5 m^2. The RO experimental set-up is shown in Figure 8. Reverse osmosis was conducted at a feed inlet pressure of 4 000 kPa (linear velocity approximately 2 m/s). Flow reversal with sponge ball cleaning (30 minutes) was applied. Clean water fluxes were determined before and after the batch runs. The RO membranes were cleaned with a 2 percent citric acid solution (pH 4,5 with ammonia) when necessary.

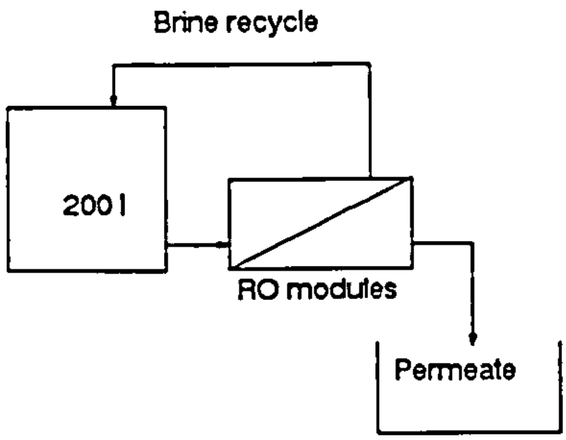

Figure 8 : RO experimental set-up for treatment of soak paddle effluent (cellulose acetate RO membranes).

A batch (100 litre) of the cross-flow microfiltered undiluted effluent (initial electrical conductivity 7160 mS/m) was batch wise desalinated in the RO unit. One batch (100 litre) of the CFMF permeate from the sump containing soak paddle effluent (see Figure 3), was also desalinated. The electrical conductivity of the RO feed, permeate and brine, temperature of the feed and permeate flux were measured as a function of time. The TDS and pH of the feed, brine and the composite permeate were also measured.

Four batches of the soak paddle effluent (after CFMF treatment) with lower electrical conductivities between 2 500 and 3 500 mS/m were also batchwise desalinated. The chemical composition of the RO feed, permeate and brine was measured on a regular basis.

3.5 Ultrafiltration reverse osmosis (UFRO) treatment of dye-house, liming and deliming effluents

Exhausted samples (200 ℓ each) from the dye-house, liming and deliming operations (see Tables 2 and 3) were batchwise treated with tubular UF (polysulphone membranes; 3,5 m^2 total membrane area). The initial feed pressure was set at 200 kPa (dye-house effluent) but was increased to 400 kPa due to the low permeate flux that was experienced. The feed pressure used for subsequent runs was 400 kPa. Flow reversal without sponge ball cleaning was used during the first run on dye-house effluent. However, flow reversal with sponge ball cleaning was used for all subsequent runs (30 min. cycle time). Clean water flux (200 kPa) was determined before and after each run. The membranes were cleaned with 1 percent Biotex solution at room temperature when necessary. Batch runs were terminated when a water recovery of approximately 90 percent was obtained. Permeate flux, temperature of feed and water recovery were measured as a function of time. The chemical composition of the UF feed was determined as well as the COD of the UF permeate and brine.

The pH of the liming (pH approximately 11) and deliming (pH approximately 11) UF permeates were reduced to a pH of approximately 6,5 with hydrochloric acid prior to batchwise tubular RO desalination (4 000 kPa; flow reversal and sponge ball cleaning) with tubular cellulose acetate RO membranes (3,5 m^2 total membrane area). Approximately 6,3 and 8,21 mℓ concentrated acid was used for the neutralization of the liming and deliming effluents, respectively. Clean water fluxes were measured before and after the batch runs and the membranes were cleaned with a one percent Biotex solution at room temperature when necessary. The RO batch runs were terminated at approximately 80 percent water recovery. The conductivity and pH of the feed, permeate and brine were measured as a function of time. The feed temperature was measured and permeate flux was determined as a function of time. The chemical composition of the RO feed, composite permeate and brine was also determined.

4. RESULTS AND DISCUSSION

4.1 Fouling potential of final effluent for tubular polysulphone ultrafiltration membranes and membrane cleaning methods

The detailed experimental data is shown in Appendix A. Permeate flux as a function of time is shown in Figure 9.

Clean water flux was determined at 2 469 ℓ/m^2.d at 200 kPa feed inlet pressure before the run was started (Figure 9). Permeate flux commenced at 580 ℓ/m^2.d (200 kPa). Flux, however, declined rapidly as a result of membrane surface fouling and was determined at 93 ℓ/m^2.d after 67 hours of operation. Clean water flux was conducted after a water rinse and was determined as 113 ℓ/m^2.d. A warm water rinse (60 - 65 °C) increased CWF dramatically. Clean water flux was determined at 457 ℓ/m^2.d after the warm water rinse. The warm water rinse was blackish in colour during cleaning. The blackish colour was given off during sponge ball reversal (5 minutes reversal) during membrane cleaning. The blackish colour was still giving being given off during the subsequent cold water rinse during sponge ball reversal (SBR) during measurement of CWF. This showed that the membranes were not completely cleaned. It is interesting to note that CWF has increased further to 1 531 ℓ/m^2.d after preservation of the membranes in a 0,1 percent sodium metabisulphite solution over the weekend. It was also observed during the initial stages of the run that the UF permeate became milky on standing.

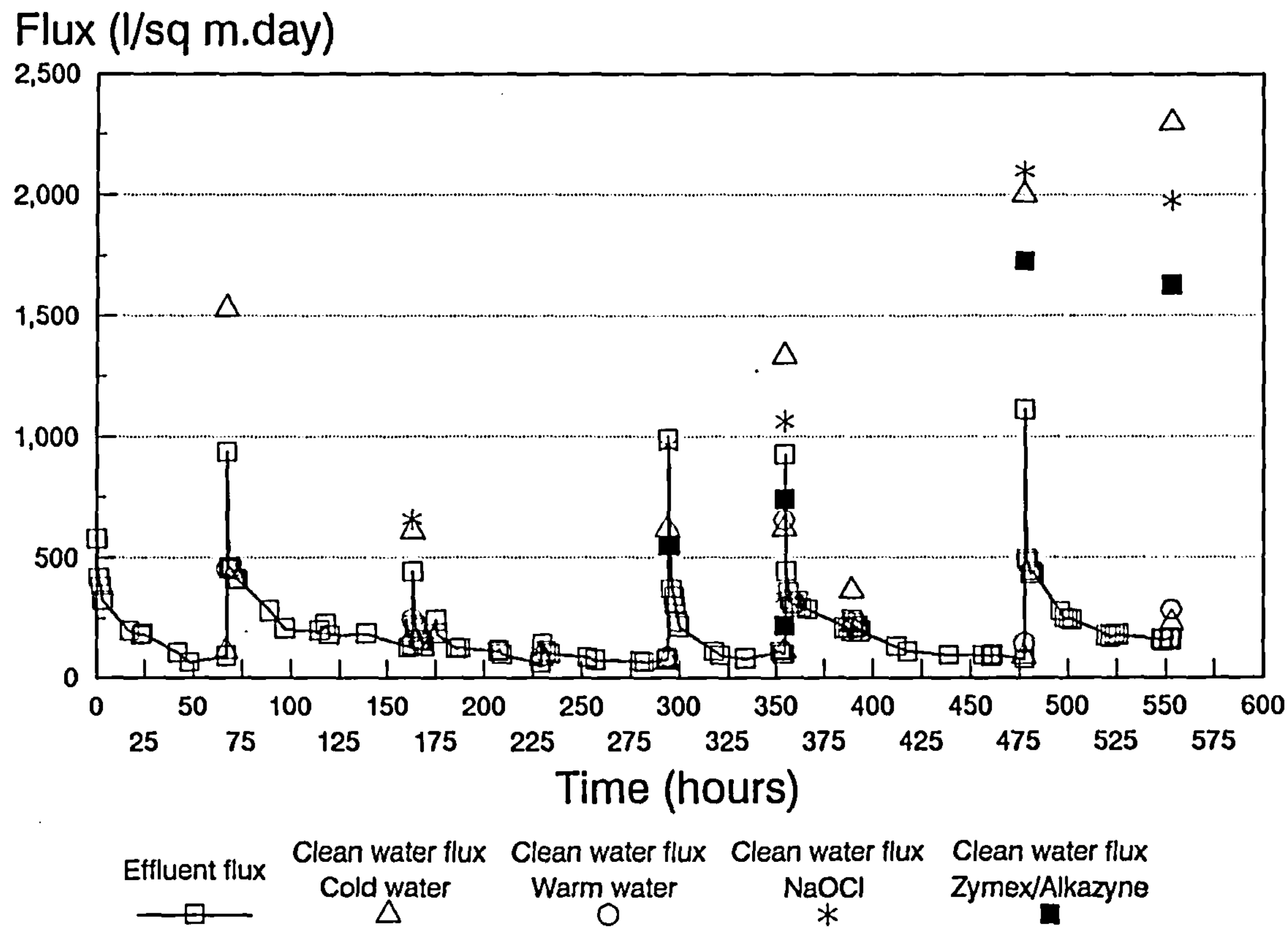

Figure 9 : Permeate flux as a function of time during treatment of final effluent with tubular polysulphone UF membranes (50 and 90% water recovery).

Permeate flux was 938 ℓ/m^2.d (after 67 hours) when the run was started and decreased to 136 ℓ/m^2.d after 163 hours of operation. A warm water rinse (70 °C), followed by cleaning of the membranes with sodium hypochlorite solution improved CWF significantly. Clean water flux increased from 181 ℓ/m^2.d before cleaning to 658 ℓ/m^2.d after cleaning. The sodium hypochlorite had a significant effect on membrane cleaning. Solid material was removed from the membranes during SBR which did not dissolve in dilute acid or alkali. The spent hypochlorite solution was slightly brown in colour. The UF brine appeared to be clean in this case during measurement of CWF. Preservation of the membranes in sodium metabisulfite solution over the weekend had no positive effect on CWF in this case.

Permeate flux was 444 ℓ/m^2.d when the run was started (after 163 hours) and decreased to 64 ℓ/m^2.d after 229 hours of operation. Clean water flux only increased from 84 to 105 ℓ/m^2.d after warm water and sodium hypochlorite cleanings. The membranes, however, were not completely cleaned because a darkish colour was given off during SBR. It is also interesting to note that the warm water rinse did not increase CWF significantly in this case. A more significant increase in CWF was obtained after the sodium hypochlorite cleaning.

Permeate flux was 142 ℓ/m^2.d when the run was started (230 hours) and decreased to 82 ℓ/m^2.d after 294 hours of operation. A warm water rinse (65 °C) followed by cleaning with detergent A increased the CWF from 68 ℓ/m^2.d to 549 ℓ/m^2.d. The membranes, however, were not completely cleaned after cleaning with detergent A because a black colour was still given off during SBR when the CWF was measured. Preservation of the membranes overnight in a 0,1 percent sodium metabisulfite solution further increased the CWF to 617 ℓ/m^2.d. Clean water flux further increased to 963 ℓ/m^2.d after a sodium hypochlorite cleaning. Therefore, it appeared that permeate flux could be significantly improved with chemical cleaning of the membranes.

Permeate flux was 987 ℓ/m^2.d when the run was started (294 hours) and decreased to 98,7 ℓ/m^2.d after 354 hours of operation. The membranes were cleaned twice with warm water, detergent A and sodium hypochlorite solution in an attempt to determine whether the CWF could be completely restored. Clean water flux increased from 111 ℓ/m^2.d to 1 333 ℓ/m^2.d (after preservation of the membranes). It appeared, however, that the membranes were still not completely cleaned after the two cleaning steps.

The pH of the UF feed water was adjusted to a pH of approximately 5 with hydrochloric acid in an attempt to determine the effect of a lower pH feed on membrane fouling and permeate flux. Permeate flux was 926 ℓ/m^2.d when the run was started (354 hours) and decreased to 78 ℓ/m^2.d after 477,5 hours of operation. A warm rinse followed by detergent A and sodium hypochlorite cleanings improved CWF from 89 ℓ/m^2.d to approximately 2 000 ℓ/m^2.d. The UF brine was also much cleaner during SBR. It therefore appeared that a lower pH feed water had a significant effect on the CWF of the membranes and to restore membrane performance after fouling.

Water recovery was increased from approximately 50 to approximately 90 percent towards the end of the run . Permeate flux was 1 111 ℓ/m^2.d (477 hours) when the run was started and decreased to 156 ℓ/m^2.d after 533 hours of operation. The membranes were cleaned with warm water, detergent A and sodium hypochlorite solution. Clean water flux increased from 222 ℓ/m^2.d to 2 296 ℓ/m^2.d after cleaning and preservation of the membranes. Therefore, it appeared that the CWF of the membranes could almost be completely restored to the initial CWF of 2 468 ℓ/m^2.d.

4.2 COD of UF feed, product and brine

The COD of the UF feed, product and brine is shown in Figure 10. The COD of the UF feed varied between approximately 1 500 and 4 000 mg/ℓ over the test period. COD removal was low. COD removals varied between approximately 6 and 32 percent. This showed that most of the organics in the effluent had a molecular mass of less than 40 000 which was the molecular mass cut-off of the UF membranes that were used for the study.

4.3 Electrical conductivity of UF feed, product and brine

The electrical conductivity of the UF feed, product and brine is shown in Figure 11. The electrical conductivity of the UF feed varied between approximately 850 and 1 800 mS/m over the test period. No salinity was removed by the UF membranes.

4.4 pH of UF feed, product and brine

The pH of the UF feed, product and brine is shown in Figure 12. The pH of the UF feed varied between approximately 6,5 and 7,2 over a 350 hour test period. The pH of the effluent, however, was reduced to approximately 5 with hydrochloric acid after 350 hours of operation. Reduction in the pH of the UF feed resulted in an almost complete restoration of the CWF of the UF membranes.

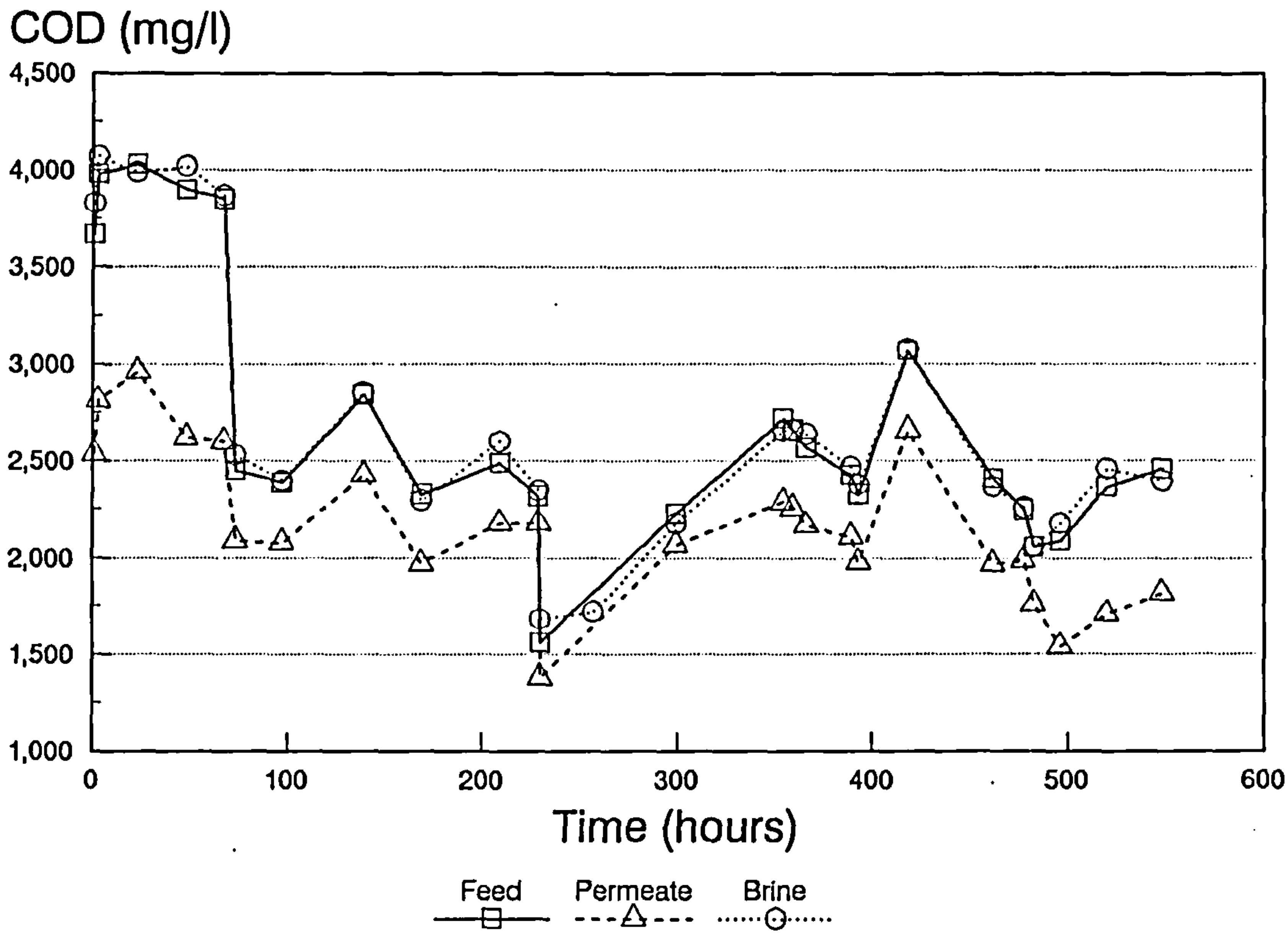

Figure 10 : COD of UF feed, product and brine as a function of time during UF treatment of the final effluent.

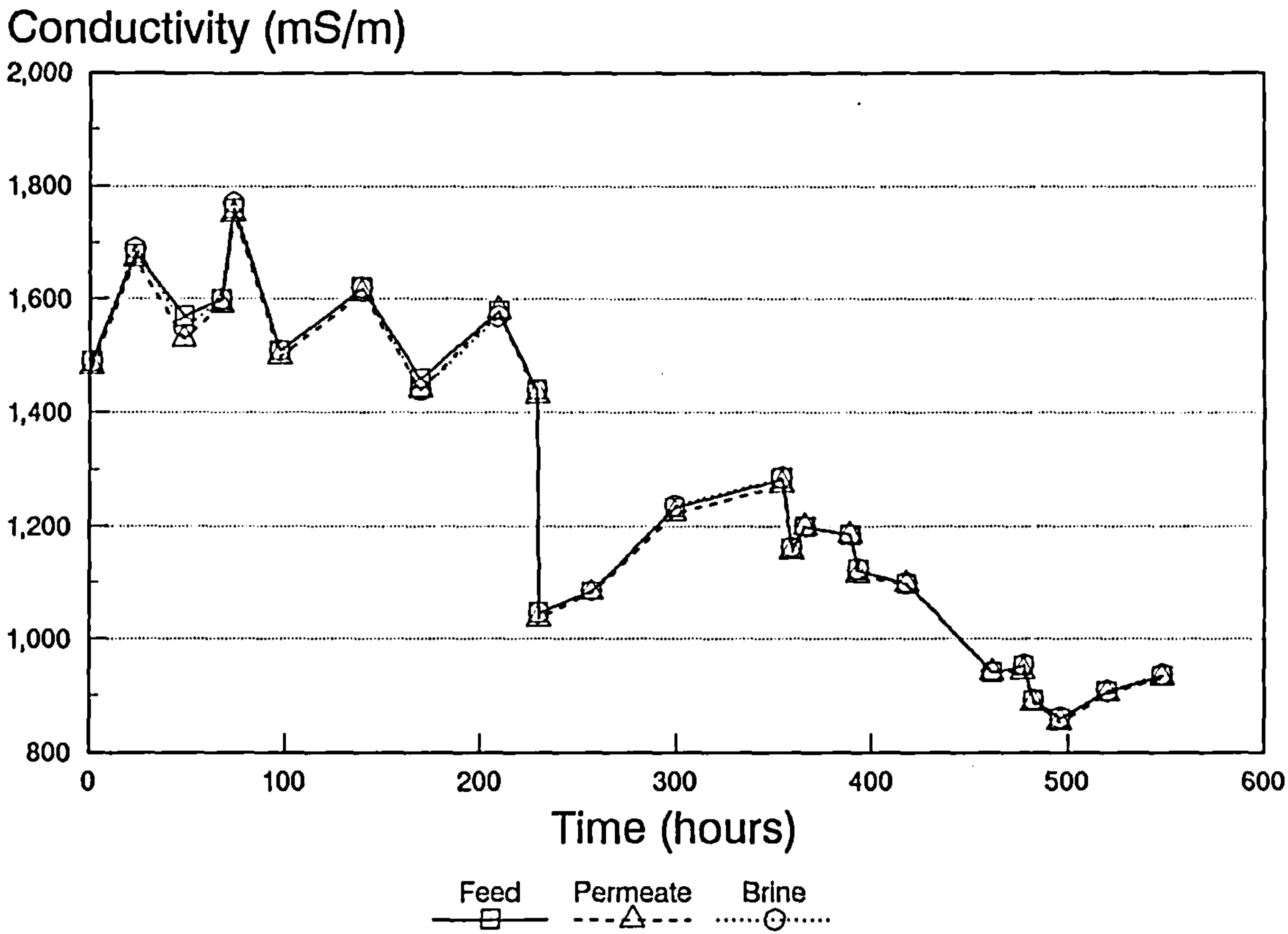

Figure 11 : Electrical conductivity of UF feed, product and brine as a function of time during UF treatment of the final effluent.

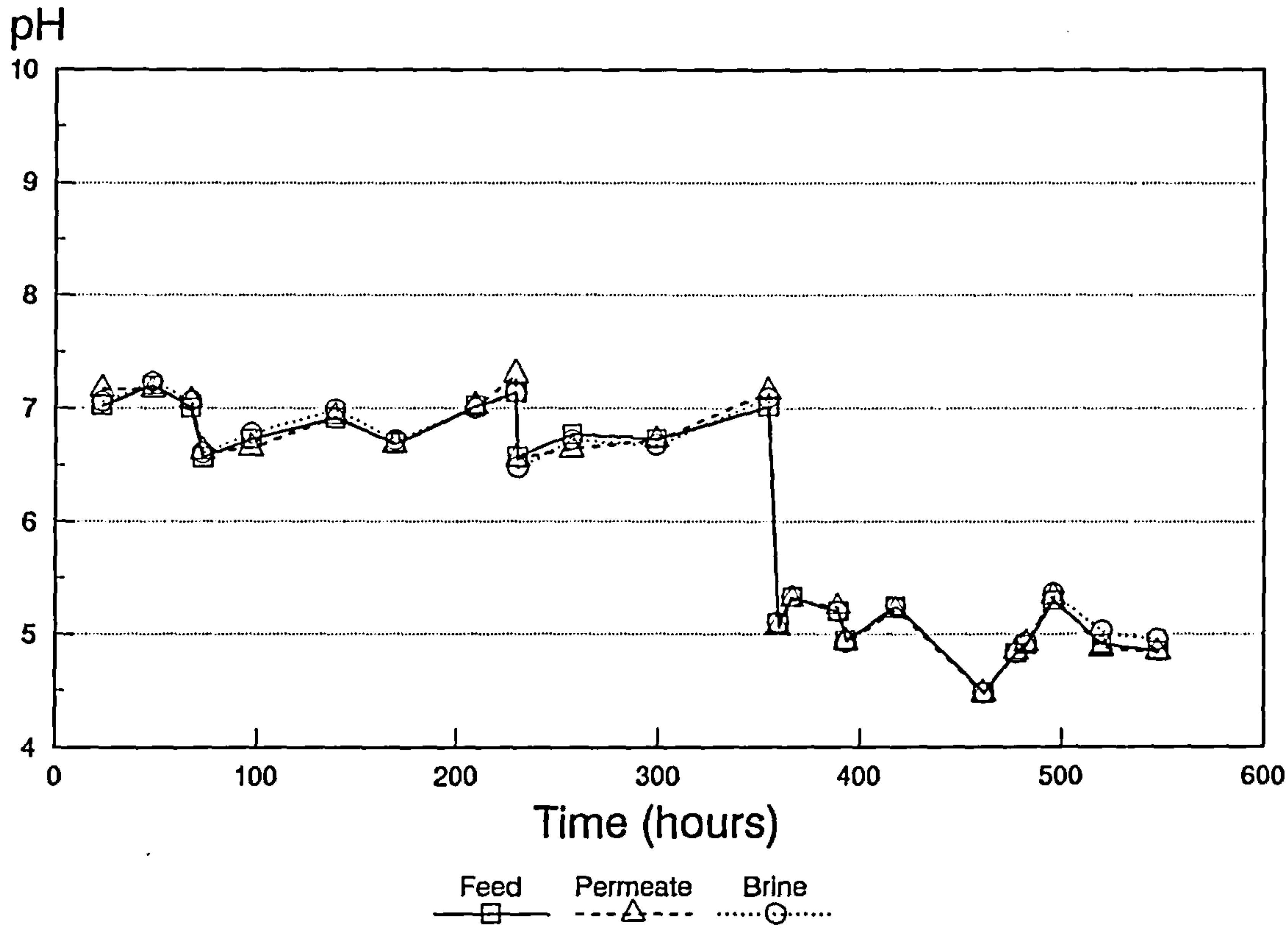

Figure 12 : pH of the UF feed, product and brine as a function of time during UF treatment of the final effluent.

4.5 Chemical composition of UF feed, product and brine

The chemical composition of the UF feed, product and brine is shown in Tables 2 to 6. The electrical conductivity of the UF feed varied between 952 and 1 570 mS/m. The concentration levels of sodium and chloride in the UF feed are high. The sodium and chloride concentration levels varied between approximately 2 800 and 5 300; and 2 300 and 7 700 mg/ℓ, respectively. COD varied between 2 230 and 3 850 mg/ℓ . Poor COD removals, however, were obtained with UF. COD removals varied between 8 and 32 percent.

Table 2 : Chemical composition of UF feed, product and brine (67 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	5 311	5 174	5 311
Potassium	100	99	98
Calcium	382	387	365
Magnesium	187	147	129
TKN as N	693,4	610,5	707,4
Ammonia as N	557	386,4	554,5
Nitrate & Nitrite as N	—	—	—
Sulphate	2 180	2 356	2 437
Chloride	7 694	7 012	6 680
Alkalinity as $CaCO_3$	753	689	439
COD	3 850	3 870	2 600
Sulphide	112	120	85
Chromium	3	3,4	0,16
Iron	24,4	25,5	1
Manganese	3,94	3,95	4,01
Conductivity (mS/m)	1 570	1 550	1 530
TDS	17 637	18 045	17 697

Table 3 : Chemical composition of UF feed, product and brine (299 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	3 487	6 941	7 591
Potassium	96	98	100
Calcium	264	259	255
Magnesium	131	130	130
TKN as N	608,3	711,6	789,6
Ammonia as N	555	594,1	783,7
Nitrate & Nitrite as N	< 0,2	< 0,2	< 0,2
Sulphate	2 093	2 017	2 176
Chloride	3 617	4 730	4 601
Alkalinity as $CaCO_3$	237	282	233
COD	2 230	2 160	2 060
Sulphide	50	65	60
Chromium	0,40	0,40	0,17
Iron	20,55	20,40	0,78
Fats and Oils	13,5	10,8	5,5
Manganese	5,05		4,7
Conductivity (mS/m)	1 233	1 236	1 222
TDS	13 868	14 103	13 632

Table 4 : Chemical composition of UF feed, product and brine (354 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	3 844	3 605	3 671
Potassium	102	105	99
Calcium	314	307	299
Magnesium	148	144	148
TKN as N	716,8	597,7	376,4
Ammonia as N	738,3	703,5	750,9
Nitrate & Nitrite as N	—	—	—
Sulphate	2 441	2 264	2 395
Chloride	4 214	4 980	4 969
Alkalinity as $CaCO_3$	985	1 095	668
COD	2 720	2 660	2 290
Sulphide	83,2	86,4	56
Chromium	1,36	1,39	0,49
Iron	14,2	14,4	2,23
Fats and Oils	—	—	—
Manganese	5,25	5,3	5
Conductivity (mS/m)	1 284	1 273	1 286
TDS	14 145	14 581	14 485

Table 5 : Chemical composition of UF feed, product and brine (366 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	3 931	3 865	3 888
Potassium	145	148	145
Calcium	279	285	282
Magnesium	146	142	146
TKN as N	716	696	654,7
Ammonia as N	571,1	492	501
Nitrate & Nitrite as N	< 0,2	< 0,2	< 0,2
Sulphate	2 538	2 507	2 357
Total phosphate	2,2	2,6	0,5
Chloride	2 278	2 338	2 273
Alkalinity as $CaCO_3$	22	8	251
COD	2 570	2 640	2 170
Sulphide	10	6	10
Chromium	1,85	1,94	0,78
Iron	41,9	42,9	37,6
Fluoride	0,8	0,8	1,4
Manganese	3,56	3,55	3,83
Conductivity (mS/m)	1 200	1 200	1 199
TDS	14 956	14 504	14 420

Table 6 : Chemical composition of UF feed, product and brine (477,5 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	2 792	2 626	2 300
Potassium	147	172	136
Calcium	305	322	313
Magnesium	145	148	147
TKN as N	505,9	497,3	520,5
Ammonia as N	455,7	475,8	497,3
Nitrate & Nitrite as N	< 0,2	0,2	< 0,2
Sulphate	2 692	2 825	2 894
Chloride	2 396	2 388	2 388
Alkalinity as $CaCO_3$	156	158	165
COD	2 250	2 260	1 990
Sulphide	22	22	18
Chromium	1,65	1,68	0,63
Iron	51,3	52,2	49,7
Fluoride	4,8	5,6	4,1
Fats and Oils	37,5	31,5	14,4
Manganese	5,2	5,3	5,2
Conductivity (mS/m)	952	954	943
TDS	11 984	12 476	11 207

The sulphide concentration level in the UF feed varied between 10 and 112 mg/ℓ. It is interesting to note that sulphides were removed to a certain extent during UF treatment of the effluent. The concentration levels of chromium, iron and manganese in the effluent are also high. Chromium, iron and manganese concentration levels in the UF feed varied between 1,4 to 3; 14,2 to 51,3; and 3,6 to 5,2 mg/ℓ, respectively. It is interesting to note that significant chromium and iron removals were obtained with UF in certain cases. It also appeared that almost no manganese was removed with UF. Manganese and other cations could form complexes with the organics in the UF feed and could pass unhindered through the UF membranes.

The ammonia-nitrogen concentration levels of the UF feed are also high. Ammonia nitrogen concentration levels varied between 455 and 778 mg/ℓ. Fats and oils varied between 13,5 and 37,5 mg/ℓ in the UF feed. Significant fat and oil removals were obtained with the UF membranes. Fats and oils and metal hydroxides, oxides and sulphides are potential membrane fouling agents. These compounds are present in the UF feed. Therefore, membrane fouling can be expected to occur.

5. ULTRAFILTRATION REVERSE OSMOSIS TREATMENT OF FINAL EFFLUENT - POLYAMIDE NANOFILTRATION REVERSE OSMOSIS MEMBRANES

5.1 Ultrafiltration permeate flux as a function of time

The detailed experimental data is shown in Appendix B. Permeate flux as a function of time is shown in Figure 13.

Permeate flux started at 1 404 ℓ/m^2.d and decreased to 216 ℓ/m^2.d after 25 hours of operation (8 m^2 membrane area). Clean water flux was measured at 277 ℓ/m^2.d and increased from 277 ℓ/m^2.d to 468 ℓ/m^2.d after a warm water rinse. Clean water flux further increased to 2 916 ℓ/m^2.d after a detergent A rinse to 3 132 ℓ/m^2.d after cleaning with a sodium hypochlorite solution. Detergent A again proved to be a very effective membrane cleaning agent. It is also interesting to note that the CWF was higher after membrane cleaning than in the beginning of the run (CWF 1 700 ℓ/m^2.d). This could be ascribed to a fouled membrane surface when the run was started because the membranes had previously been used.

Permeate flux was high (1 782 ℓ/m^2.d) when the run was started and decreased to 450 ℓ/m^2.d after approximately 50 hours of operation. Clean water flux was determined at 756 ℓ/m^2.d and increased to 864; 2 160 and 2 592 ℓ/m^2.d after warm water, detergent A and sodium hypochlorite rinses, respectively. Clean water flux (after cleaning) however, could not be restored to the flux that was obtained after the previous cleaning cycle. This showed that membrane fouling took place and that the membranes were not properly cleaned.

Permeate flux was 677 ℓ/m^2.d when the run was started at 51,5 hours of operation and decreased to 374 ℓ/m^2.d after 67,5 hours of operation. Clean water flux was determined at 439 ℓ/m^2.d. Clean water fluxes after warm water, detergent A and sodium hypochlorite rinses increased to 1 102; 1 771 and 1 879 ℓ/m^2.d, respectively. The clean water fluxes after the third cleaning cycle were again lower than during the previous cleaning cycles. This showed that the membranes were not completely cleaned. Multiple cleaning, however, should restore the CWF completely.

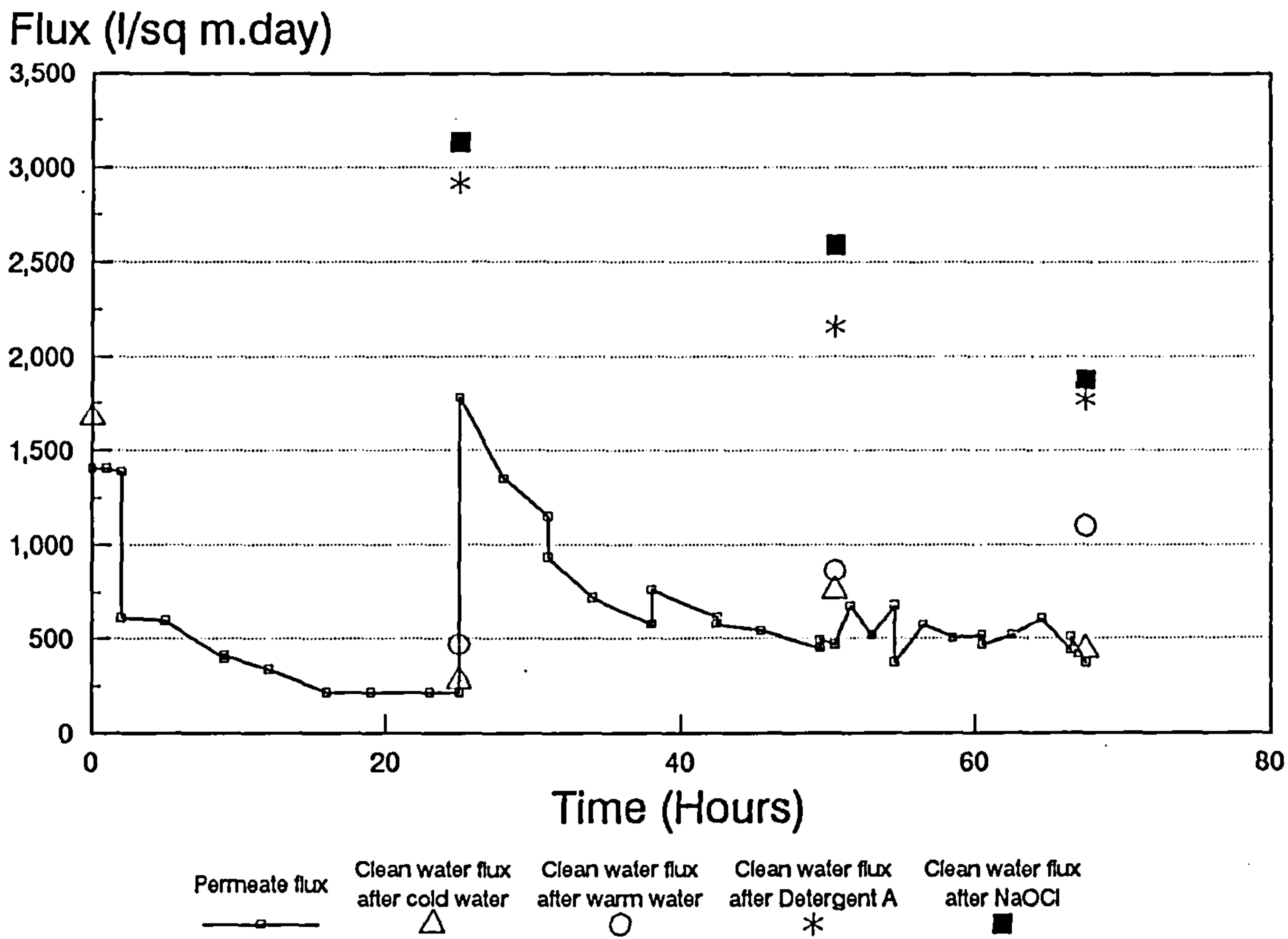

Figure 13 : UF permeate flux as a function of time during UFRO treatment of the final effluent (polysulphone UF membranes).

5.2 Reverse osmosis permeate flux as a function of time

The detailed experimental data is shown in Appendix C. Permeate flux as a function of time is shown in Figure 14.

Permeate flux was 286 ℓ/m^2.d when the run was started and decreased to 96,5 ℓ/m^2.d after 25 hours of operation (0,875 m^2 membrane area). This rapid decline in permeate flux was unexpected because ultrafiltered water was used as feed for the RO membranes. Clean water flux was determined at 142 ℓ/m^2.d and the CWF increased to 154 ℓ/m^2.d and 159 ℓ/m^2.d after citric and Biotex rinses, respectively. Therefore, it appeared that the membranes were fouled.

Permeate flux was 179 ℓ/m^2.d when the run was commenced after 25 hours of operation and again rapidly decreased to 91 ℓ/m^2.d after 38 hours of operation. Clean water flux was determined at 145 ℓ/m^2.d and increased to 257 ℓ/m^2.d after the membranes were cleaned with detergent A. Therefore, it appeared that the CWF of the RO membranes could be significantly increased with a detergent A cleaning.

Permeate flux was 144 ℓ/m^2.d when the run was started after 38 hours of operation and decreased to 85 ℓ/m^2.d after 49,5 hours of operation. The membranes were then cleaned with P3 Ultrasil 50 cleaning agent and CWF increased from 116 ℓ/m^2.d to 145 ℓ/m^2.d. The membranes, however, were not completely cleaned.

Permeate flux was 151 ℓ/m^2.d when the run was started and decreased to 90 ℓ/m^2.d when the run was terminated after approximately 70 hours of operation. Clean water flux increased from 104 ℓ/m^2.d to only 121 ℓ/m^2.d after the membranes were cleaned with detergent A only. The membranes were not rinsed with warm water prior to cleaning with detergent A in this case. This might explain the low CWF that was obtained after cleaning of the membranes with detergent A. (Note: water recovery was approximately 80 percent).

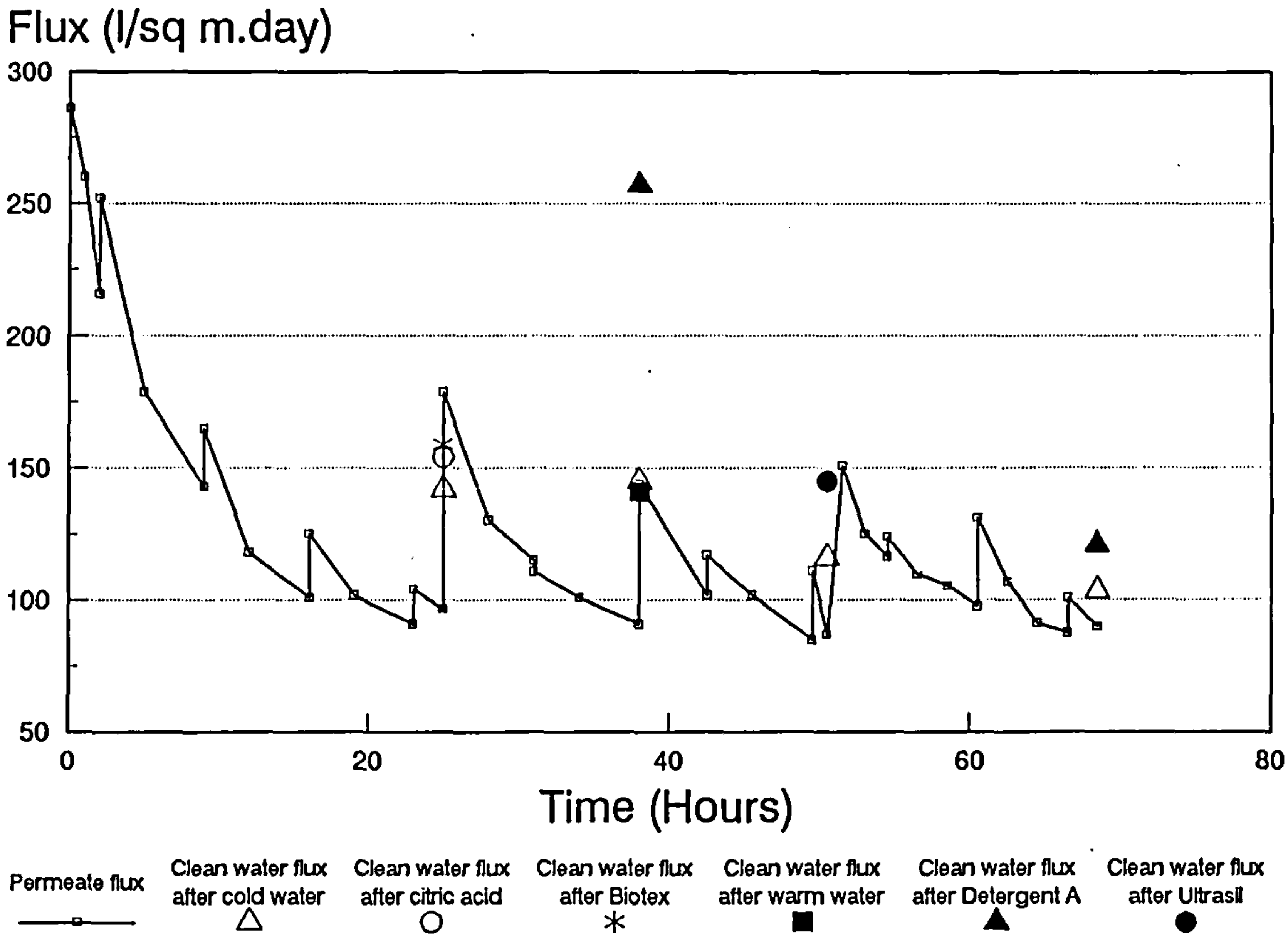

Figure 14 : RO permeate flux as a function of time during UFRO treatment of the final effluent (PCI AFC 30 polyamide nanofiltration RO membranes)

5.3 Electrical conductivity of RO feed, permeate and brine

The electrical conductivity of the RO feed permeate and brine is shown in Table 7 and Figure 15. The feed electrical conductivity varied between 600 and 2 500 mS/m. The electrical conductivity of the RO permeate varied between 500 and 1 500 mS/m. The electrical conductivity removal from the RO feed varied between 29 and 37 percent. The nanofiltration RO membranes have a relatively low rejection for monovalent ions and a relatively high rejection for divalent ions. The majority of ions present in the effluent are monovalent. Consequently, the overall salt rejection will be low. However, a higher overall removal of electrical conductivity was expected. The low electrical conductivity removal might be ascribed to membrane fouling. Nanofiltration RO membranes, on the other hand, will only be able to desalinate the effluent partially.

Table 7 : Conductivity of RO feed, permeate and brine.

Time (hours)	Conductivity (mS/m)			Conductivity Rejection (%)
	Feed	Brine	Permeate	
2	672	672	446	33,63
9	989	980	653	33,97
16	1 063	1 066	699	34,24
23	1 055	1 063	677	35,83
25	1 780	1 810	1 191	33,09
31	1 520	1 530	846	44,34
38	1 700	1 720	1 074	36,82
42,5	1 950	1 960	1 283	34,21
49,5	2 240	2 240	1 470	34,38
51,5	2 240	2 230	1 490	33,48
54,0	2 270	2 270	1 580	30,4
60,5	2 390	2 420	1 700	28,87
66,5	2 570	2 580	1 620	36,97
68,5	2 290	2 300	1 590	30,57

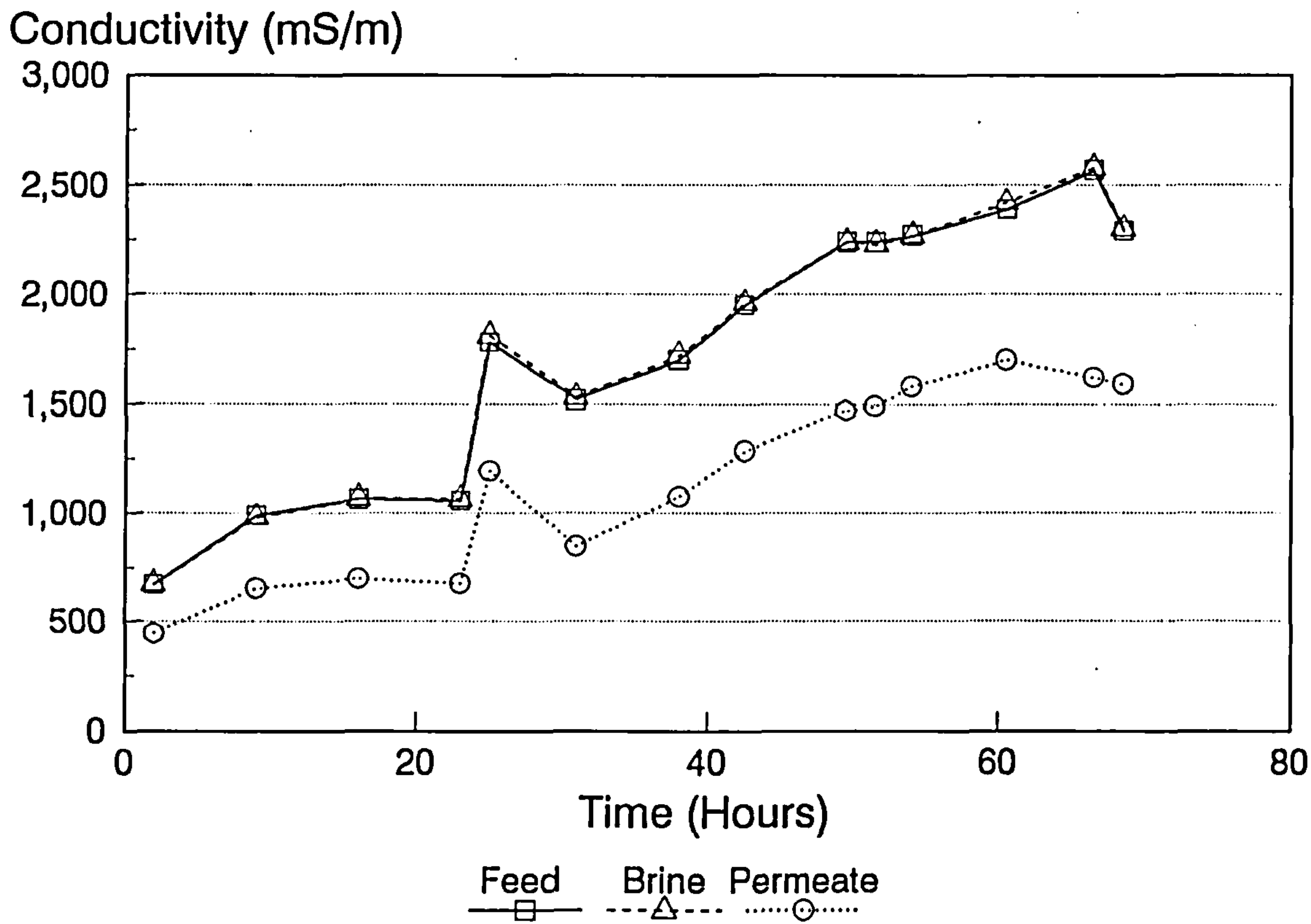

Figure 15 : Electrical conductivity of RO feed, permeate and brine during RO treatment of the final effluent.

5.4 COD of ultrafiltration and reverse osmosis feed, permeate and brine

The COD removal during UF and RO treatment of the effluent is shown in Tables 8 and 9, respectively. The COD removal during RO treatment of the UF permeate is shown in Figure 16.

The COD removal during UF treatment was very low (Table 8). COD removal varied between 0,6 and 9,6 percent. COD removal on the other hand, during RO treatment was much higher. The COD of the RO feed varied between 1 250 and 2 300 mg/ℓ. Permeate feed concentration level varied between 600 and 900 mg/ℓ. COD removals varied between 20 and 66 percent (Table 9; Figure 16).

Table 8 : COD of UF feed, permeate and brine.

Time (hours)	Chemical Oxygen Demand (mg/ℓ)			COD Rejection (%)
	Feed	Brine	Permeate	
16	1 660	1 700	1 580	4,82
23	1 610	1 650	1 600	0,62
25	1 520	1 066	1 420	6,58
31	1 540	1 063	1 510	1,95
38	1 770	1 810	1 670	5,65
42,5	1 760	1 530	1 700	3,41
49,5	1 830	1 720	1 680	8,20
51,5	1 810	1 960	1 740	3,87
54,0	1 560	2 240	1 410	9,6
60,5	1 530	2 230	820	-
66,5	1 470	2 270	1 430	2,7
68,5	2 530	2 420	1 490	2,6

Table 9 : COD of RO feed, permeate and brine.

Time (hours)	Chemical Oxygen Demand (mg/ℓ)			COD Rejection (%)
	Feed	Brine	Permeate	
2	1 170	1 270	620	47,01
9	1 830	1 820	907	50,44
16	2 100	2 140	964	54,10
23	2 270	2 210	930	59,03
25	2 140	2 030	950	55,61
31	1 660	1 680	560	66,27
38	2 030	2 010	870	57,14
42,5	2 130	2 160	910	57,28
49,5	2 250	2 230	880	60,89
51,5	2 360	2 200	930	60,59
54,0	1 630	1 660	810	50,3
60,5	1 770	1 460	1420	19,7
66,5	1 870	1 930	920	46,0
68,5	1 880	1 940	900	52,1

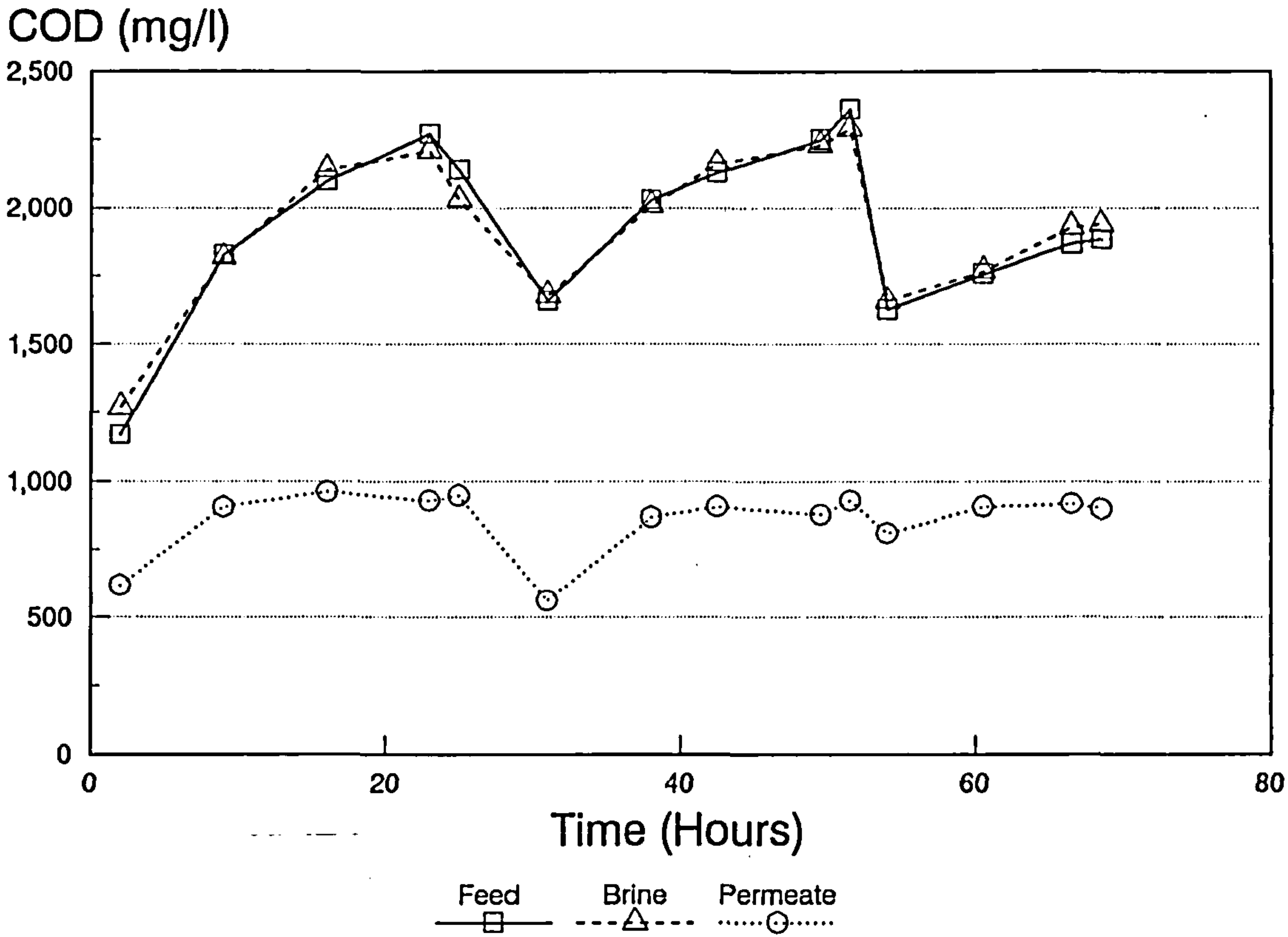

Figure 16 : COD of RO feed, permeate and brine.

5.5 Chemical composition of UF and RO feed, permeate and brine

Typical chemical compositions of the UF and RO feed, product and brine are shown in Tables 10 to 12.

Table 10 : Chemical composition of UF feed, permeate and brine (25 hours)

Constituents (mg/ℓ)	UF Feed	UF Brine	UF Product
Sodium	2 480	2 600	2 520
Potassium	86	86	86
Calcium	286	292	286
Magnesium	135,7	135,3	134,6
TKN as N	535,4	674,6	664,7
Ammonia as N	460,2	500	461,2
Nitrate & Nitrite as N	< 0,2	< 0,2	< 0,2
Sulphate	2 308	2 533	2 262
Chloride	4 371	4 462	4 049
Alkalinity as $CaCO_3$	267	330	238
COD	1 520	1 610	1 420
Sulphide	9,6	9,6	3,2
Chromium	0,34	0,4	0,10
Iron	24,6	25,5	23,7
Fluoride	3,6	3,3	3,9
Manganese	5	4,3	5
Conductivity (mS/m)	1 460	1 480	1 460
TDS	11 363	12 229	10 716

Low COD removals were obtained with UF of the effluent (Figure 10). Low electrical conductivity removals were also obtained with the nanofiltration RO membranes that were used for the study (Tables 11 and 12). Conductivity removal was approximately 34 percent. Poor sodium (40 to 71%) and chloride (12 to 22%) removals were obtained while the sulphate (84 to 97%) removals were much better. This was expected because divalent ions were much better removed than monovalent ions with nanofiltration RO membranes. However, poor removals were also obtained of other divalent ions like calcium (60 to 62%) and magnesium (64 to 68%). This might be ascribed to membrane fouling. Chromium were effectively removed (90 to 93%) while moderate removals of iron (55 and 66%) and manganese (61 and 63%) were obtained. COD removal was 50 and 61 percent. This showed that a large fraction of the organics was not removed by the membranes.

Table 11 : Chemical composition of RO feed, product and brine (9 hours)

Constituents (mg/ℓ)	Feed	Brine	Permeate	Rejection %
Sodium	6 343	6 360	1 832	71,12
Potassium	125	130	81	35,20
Calcium	278	278	105	62,23
Magnesium	139	143	45	67,63
TKN as N	469,9	494,5	463,4	1,17
Ammonia as N	469,2	462,5	412,6	12,06
Nitrate & Nitrite as N	0,4	0,4	0,4	0,0
Sulphate	3 596	3 789	577	83,95
Chloride	2 824	3 286	2 495	11,65
Alkalinity as $CaCO_3$	236	260	191	19,07
COD	1 830	1 820	907	50,44
Sulphide	< 0,1	1,6	< 0,1	0,00
Chromium	0,29	0,29	< 0,03	89,66
Iron	56,1	56,2	25,4	54,72
Fluoride	2,7	1,1	1,9	29,63
Fats and Oils	55,5	75,9	14,9	-
Manganese	7,4	7,35	2,91	60,68
Conductivity (mS/m)	989	980	653	33,97
TDS	12 676	12 623	6 471	48,95

Table 12 : Chemical composition of RO feed, product and brine (50,5 hours)

Constituents (mg/ℓ)	Feed	Brine	Permeate	Rejection %
Sodium	4 370	4 390	2 710	37,99
Potassium	116	119	65	43,97
Calcium	568	562	226	60,21
Magnesium	210	208	7,5	64,29
TKN as N	588,4	587,5	349,7	40,57
Ammonia as N	533,3	371,2	292,4	45,17
Nitrate & Nitrite as N	< 0,2	< 0,2	< 0,2	0,0
Sulphate	6 013	6 295	152	97,47
Chloride	6 171	6 280	4 789	22,40
Alkalinity as $CaCO_3$	208	250	122	41,35
COD	2 360	2 290	930	60,59
Chromium	1,5	1,2	0,1	93,33
Iron	75,7	74,1	25,9	65,79
Fluoride	4,3	5	1,1	74,42
Manganese	10,4	10,2	3,9	62,50
Conductivity (mS/m)	2 240	1 490	2 230	33,48
TDS	18 813	18 987	10 093	46,35

6. ULTRAFILTRATION REVERSE OSMOSIS TREATMENT OF FINAL EFFLUENT-CELLULOSE ACETATE REVERSE OSMOSIS MEMBRANES

6.1 Ultrafiltration permeate flux as a function of time

The detailed experimental data is shown in Appendix C. The UF permeate flux as a function of time is shown in Figure 17.

The CWF of the membranes was determined at 1 900 ℓ/m^2.d before the run was started. Permeate flux started at 680 ℓ/m^2.d and decreased to 314 ℓ/m^2.d after 14 hours of operation. The CWF was determined at 454 ℓ/m^2.d. Therefore, the CWF was reduced significantly after 14 hours of operation showing that membrane fouling had taken place.

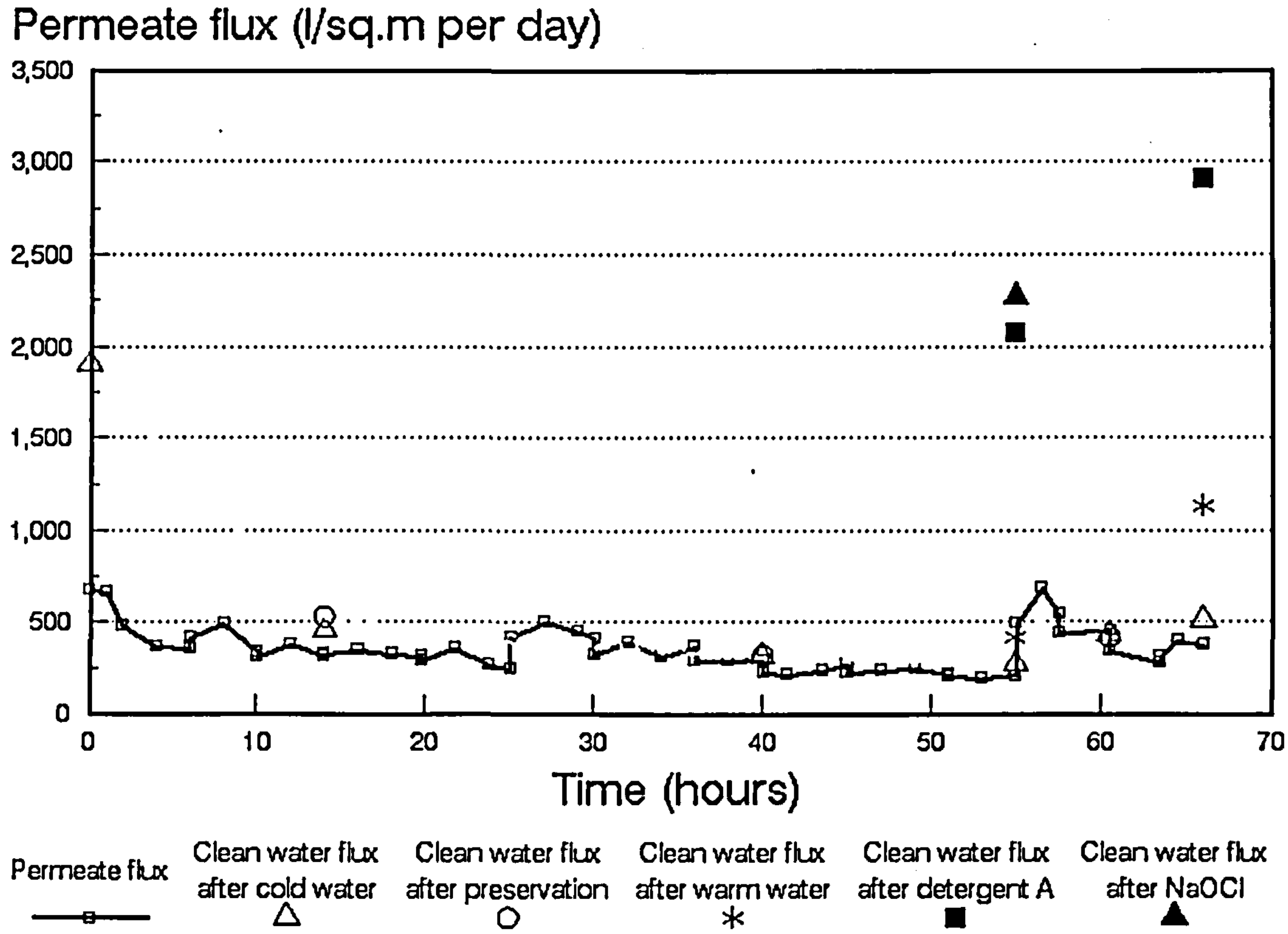

Figure 17 : UF permeate flux as a function of time during UFRO treatment of the final effluent (polysulphone UF membranes).

Preservation of the membranes in 0,1 percent sodium metabisulphite solution over the weekend improved CWF to only 529 ℓ/m^2.d.

Permeate flux was 324 ℓ/m^2.d when the run was commenced and remained more or less constant between 14 and 40 hours of operation. Permeate flux was 297 ℓ/m^2.d after 40 hours of operation. Clean water flux was determined at 313 ℓ/m^2.d. Therefore, CWF decreased from 453 ℓ/m^2.d (after 14 hours) to 313 ℓ/m^2.d after 40 hours of operation. This again showed that membrane fouling was taking place.

Permeate flux started at 227 ℓ/m^2.d when the run was commenced after 40 hours of operation and decreased to 211 ℓ/m^2.d after 55 hours of operation. The CWF was now determined at 270 ℓ/m^2.d. Therefore, CWF was further reduced — from 313 ℓ/m^2.d after 40 hours of operation to 270 ℓ/m^2.d after 55 hours of operation. A warm water rinse (approximately 70 °C) increased CWF to 410 ℓ/m^2.d. Cleaning of the membranes with detergent A and sodium hypochlorite solution improved the CWF to 2 073 and 2 668 ℓ/m^2.d, respectively. Therefore, CWF could be improved significantly with chemical cleaning.

Permeate flux was 497 ℓ/m^2.d when the run was commenced after 55 hours of operation and decreased to 378 ℓ/m^2.d after 66 hours of operation. Clean water flux was determined at 508 ℓ/m^2.d. Therefore, the CWF had increased significantly since the last cleaning - from 270 ℓ/m^2.d to 508 ℓ/m^2.d. A warm water (65 °C) and detergent A cleaning (70 °C) increased CWF further to 1 134 and 2 916 ℓ/m^2.d, respectively. Therefore, it again appeared that it should be possible to control membrane fouling with regular chemical cleaning.

6.2 Reverse osmosis permeate flux as a function of time

The RO permeate flux as a function of time is shown in Figure 18. Clean water flux was 513 ℓ/m^2.d when the run was commenced (Appendix C). The RO permeate flux was 375 ℓ/m^2.d when the run was started and decreased to 118 ℓ/m^2.d after 134 hours of operation. This decline in permeate can be ascribed to membrane fouling. Membrane fouling was again not expected because ultrafiltered effluent was used as feed to the RO membranes. Flow reversal with sponge ball cleaning was applied every 20 minutes. However, membrane fouling took place and an attempt was made to clean the fouled RO membranes.

The CWF of the membranes was determined at 288 ℓ/m^2.d after 134 hours of operation. Therefore, the CWF has decreased from 513 ℓ/m^2.d in the beginning of the run to 288 ℓ/m^2.d after 134 hours of operation. A citric acid cleaning increased CWF to 319 ℓ/m^2.d and CWF was further increased to 392 ℓ/m^2.d after cleaning of the membranes

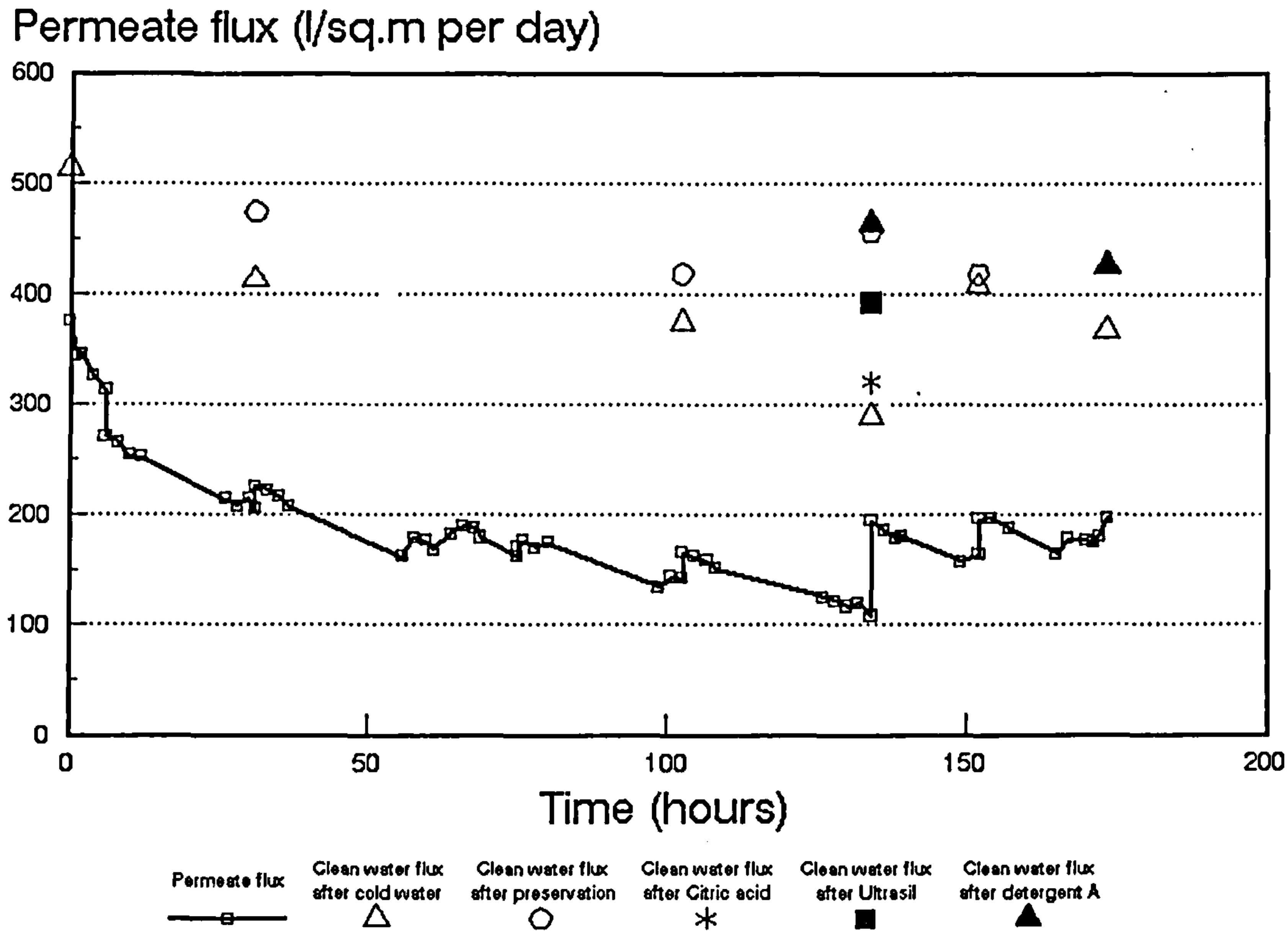

Figure 18 : RO permeate flux as a function of time during UFRO treatment of the final effluent (cellulose acetate RO membranes)

with P3 Ultrasil 50. Cleaning of the membranes with detergent A increased CWF further to 463 ℓ/m^2.d. Therefore, it appeared that CWF could almost be restored to its initial value of 513 ℓ/m^2.d.

Permeate flux was determined at 194 ℓ/m^2.d when the run was started after 134 hours of operation. Clean water flux was 407 ℓ/m^2.d after 152 hours of operation and the RO permeate flux was 197 ℓ/m^2.d when the run was commenced and decreased to 180 ℓ/m^2.d when the run was terminated after 173,5 hours of operation. Clean water flux was determined at 367 ℓ/m^2.d and increased to 426 ℓ/m^2.d after the membranes were cleaned with detergent A. Clean water flux, however, was not completely restored. However, it appeared that it should be possible to control membrane fouling with regular chemical cleaning of the membranes.

6.3 Water recoveries

Water recovery during the UFRO run is shown in Figure 19. Water recoveries during UF and RO treatment were approximately 80 and 70 percent, respectively.

6.4 Electrical conductivity of RO feed, permeate and brine

The electrical conductivity of the RO feed, brine and permeate during the UFRO run is shown in Figure 20. The feed water conductivity varied between 2 580 and 4 290 mS/m (Fig. 20 and Appendix C). Brine conductivity was only slightly higher. Permeate electrical conductivity varied between 300 and 753 mS/m during the test run (approximately 83 to 88% conductivity removal). Therefore, a relatively good quality water could be produced with RO. The electrical conductivity of the RO permeate also remained reasonably constant over the test period showing that severe membrane fouling was not taking place.

The electrical conductivity of the UF feed, brine and permeate is shown in Figure 21. The UF feed water electrical conductivity varied between 1 510 and 2 540 mS/m during the test run. The high electrical conductivity value after approximately 20 hours was caused by an acid overdose. Therefore feed, electrical conductivity varied between 1 510 and 1 860 mS/m during the run. No salinity was removed with UF.

6.5 COD of the UF and RO feed, permeate and brine

The COD of the UF and RO feed, permeate and brine is shown in Figures 22 and 23, respectively (Appendix C). The COD of the UF feed varied between 1 724 and 2 330 mg/ℓ. The COD of the UF permeate varied between 1 530 and 2 260 mg/ℓ during the run.

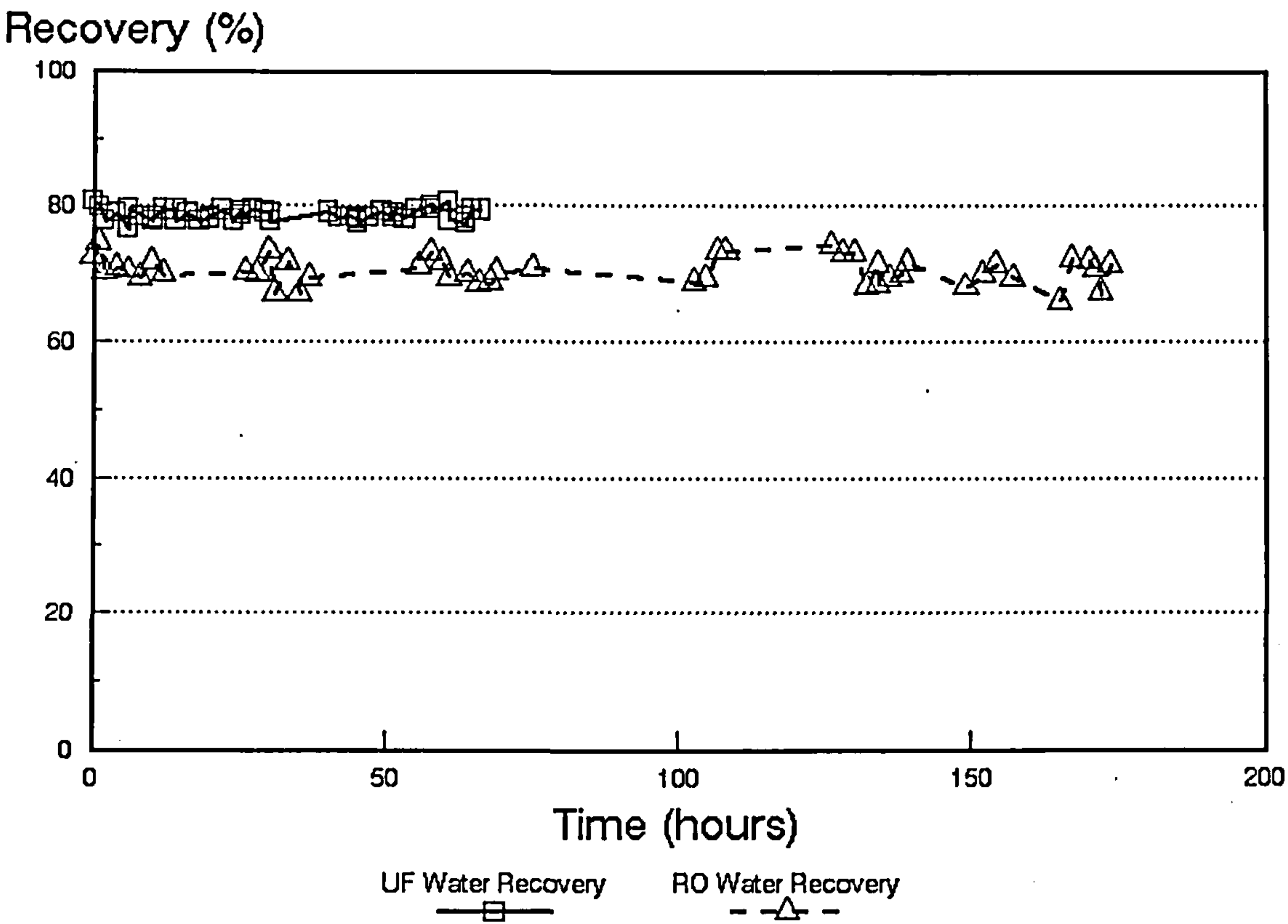

Figure 19 : Water recovery as a function of time during UFRO treatment of the final effluent.

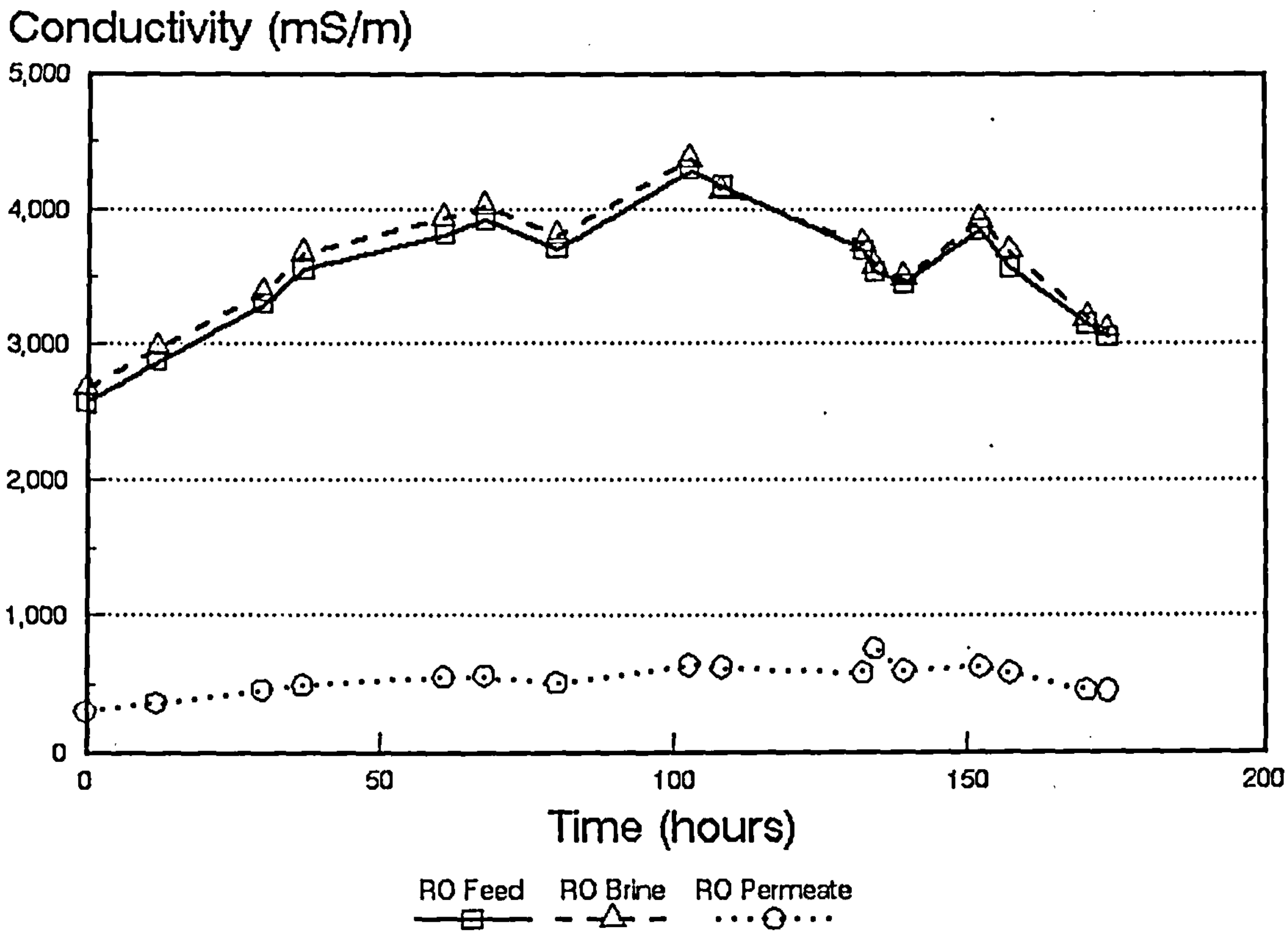

Figure 20 : Electrical conductivity of RO feed, brine and permeate as a function of time during UFRO treatment of the final effluent

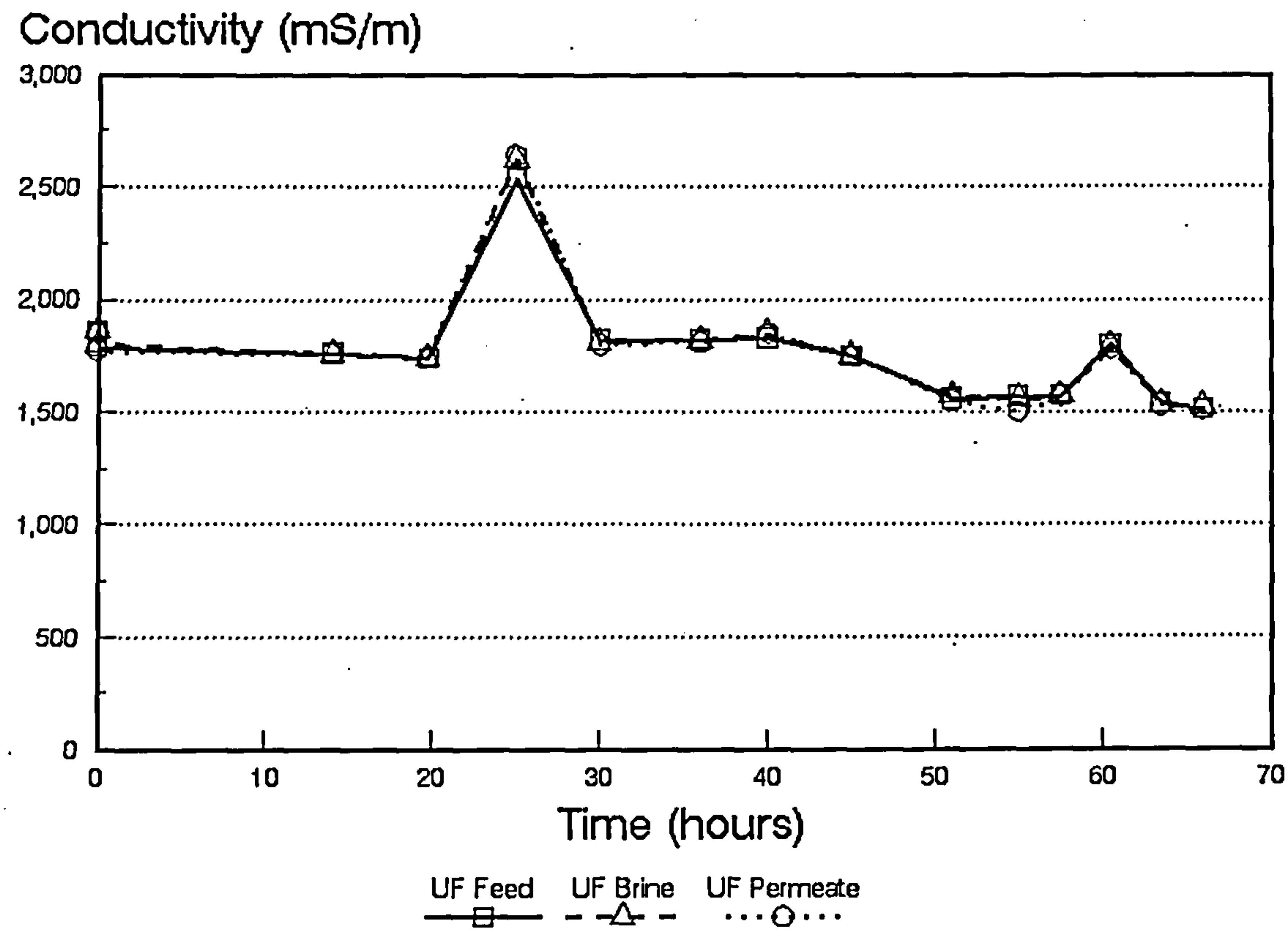

Figure 21 : Electrical conductivity of UF feed, brine and permeate as a function of time during UFRO treatment of the final effluent.

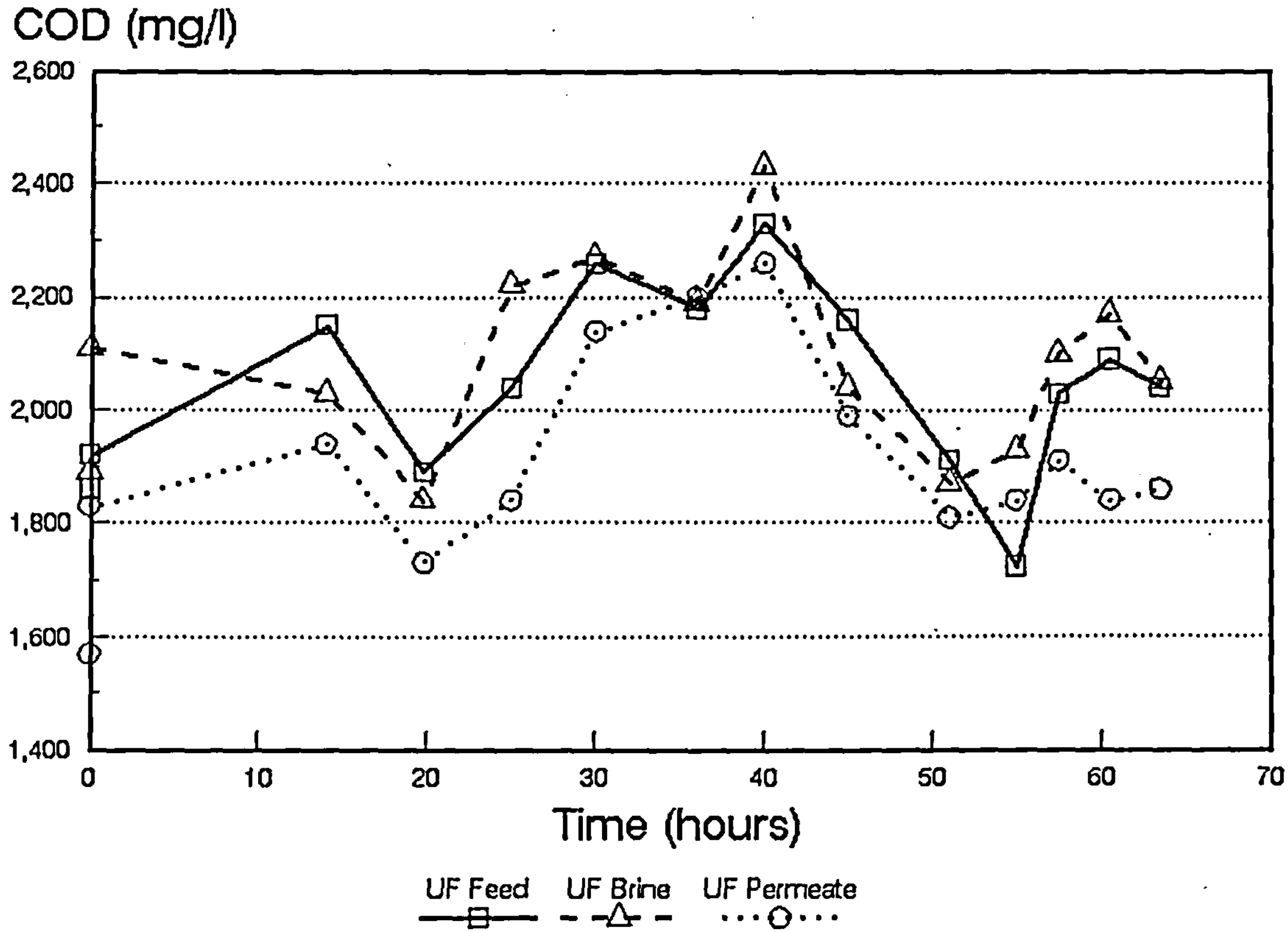

Figure 22 : COD of UF feed, brine and permeate as a function of time during UFRO treatment of the final effluent.

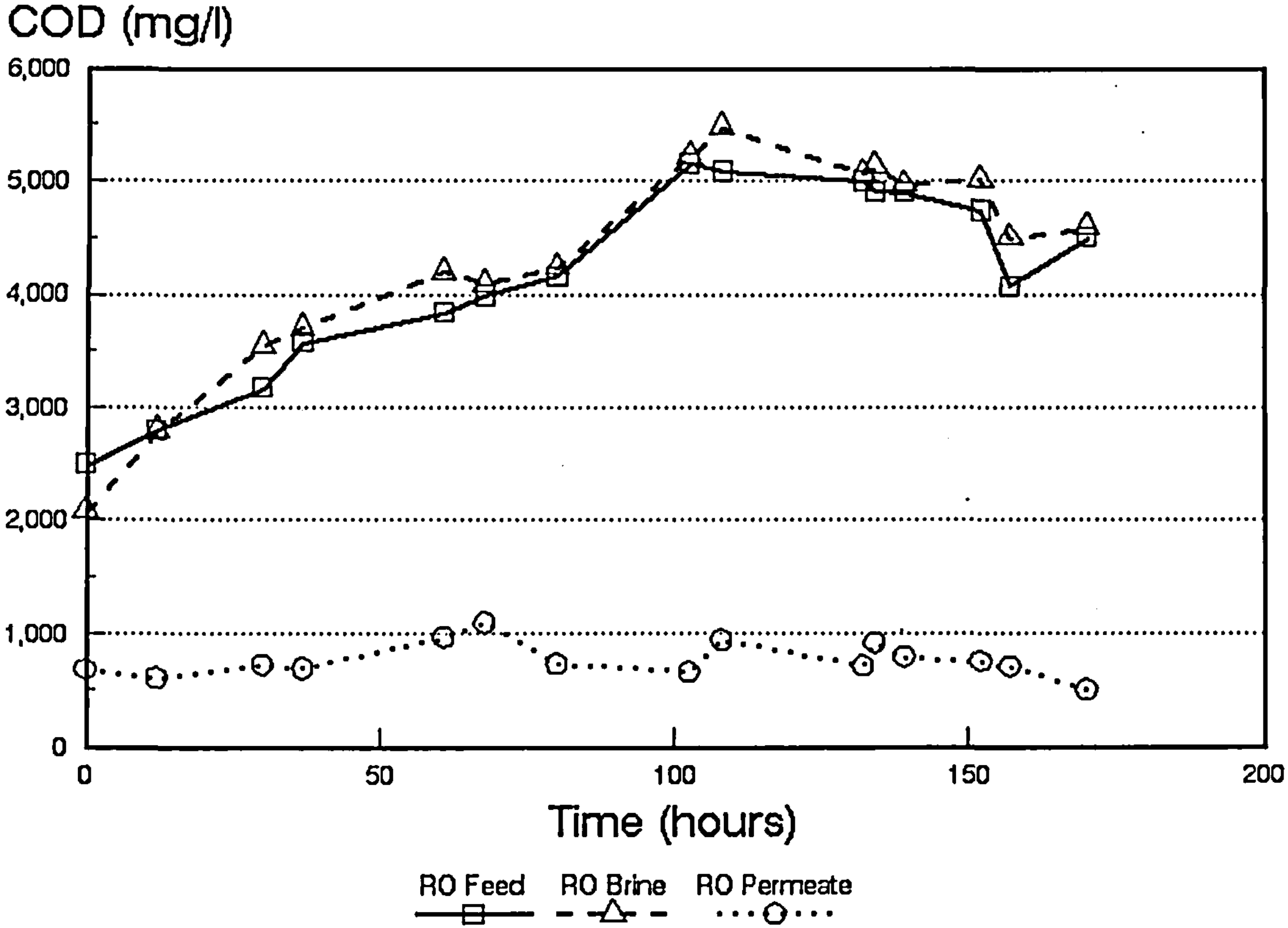

Figure 23 : COD of RO feed, brine and permeate as a function of time during UFRO treatment of the final effluent.

Therefore very little organics was removed with UF.

The COD of the RO feed varied between 2 500 and 5 160 mg/ℓ. The COD of the RO permeate varied between 500 and 1 090 mg/ℓ during the run. Therefore, relatively good organics removal was obtained with RO treatment of the effluent. However, a significant amount of low molecular mass organic compounds were not removed by RO.

6.6 Electrical conductivity and COD removal

The electrical conductivity and COD removals of the ions and organics are shown in Figure 24 (Appendix C). Electrical conductivity removal varied between 79 and 88 percent during the run. However, conductivity removal was approximately 85 percent for most of the time. Electrical conductivity removals between approximately 90 and 95 percent are usually obtained with tubular cellulose acetate RO membranes. The lower removals that were experienced could be ascribed to a partly fouled membrane surface. It is also interesting to note that electrical conductivity removal remains almost constant during the run. This showed that serious membrane fouling was not experienced.

The COD rejection varied between 72 and 90 percent during the run. Therefore, excellent COD removals were obtained with the cellulose acetate RO membranes. Much better COD removals were obtained than with the nanofiltration RO membranes.

6.7 pH of UF and RO feed, brine and permeate

The pH of the UF and RO feed, permeate and brine is shown in Figures 25 and 26. The pH of the UF feed was adjusted to a pH of approximately 5 with hydrochloric acid. The dip in the pH (Fig. 25) was caused by an acid overdose. The pH of the feed, brine and permeate was about the same.

The pH of the RO feed varied between 4,5 and 5,5 during the run (Fig. 26). The pH of the brine was about the same as that of the feed. The pH of the RO permeate, however, was lower (pH 3,7 to 4,6). The lower pH of the RO permeate can be ascribed to the passage of carbon dioxide through the RO membranes.

6.8 Chemical composition of UF and RO feed, permeate and brine

The chemical composition of the UF and RO feed, permeate and brine is shown in Tables 13 and 14; and 15 and 16, respectively. Poor COD removals were obtained with UF treatment of the effluent (Tables 13 and 14). It is interesting to note that the calcium concentration level of the UF feed is high. The calcium concentration levels in two cases

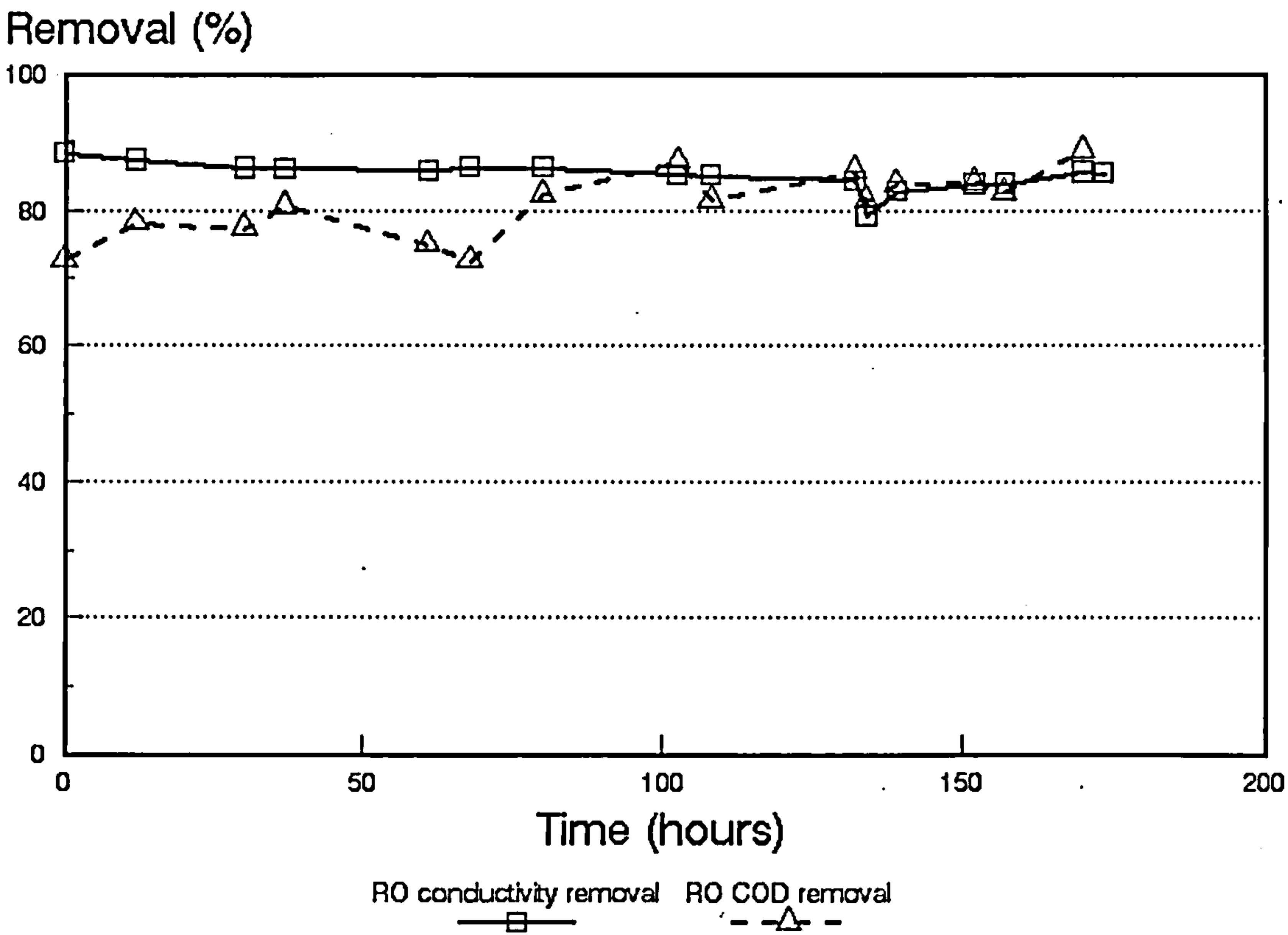

Figure 24 : Electrical conductivity and COD removal as a function of time during UFRO treatment of the final effluent.

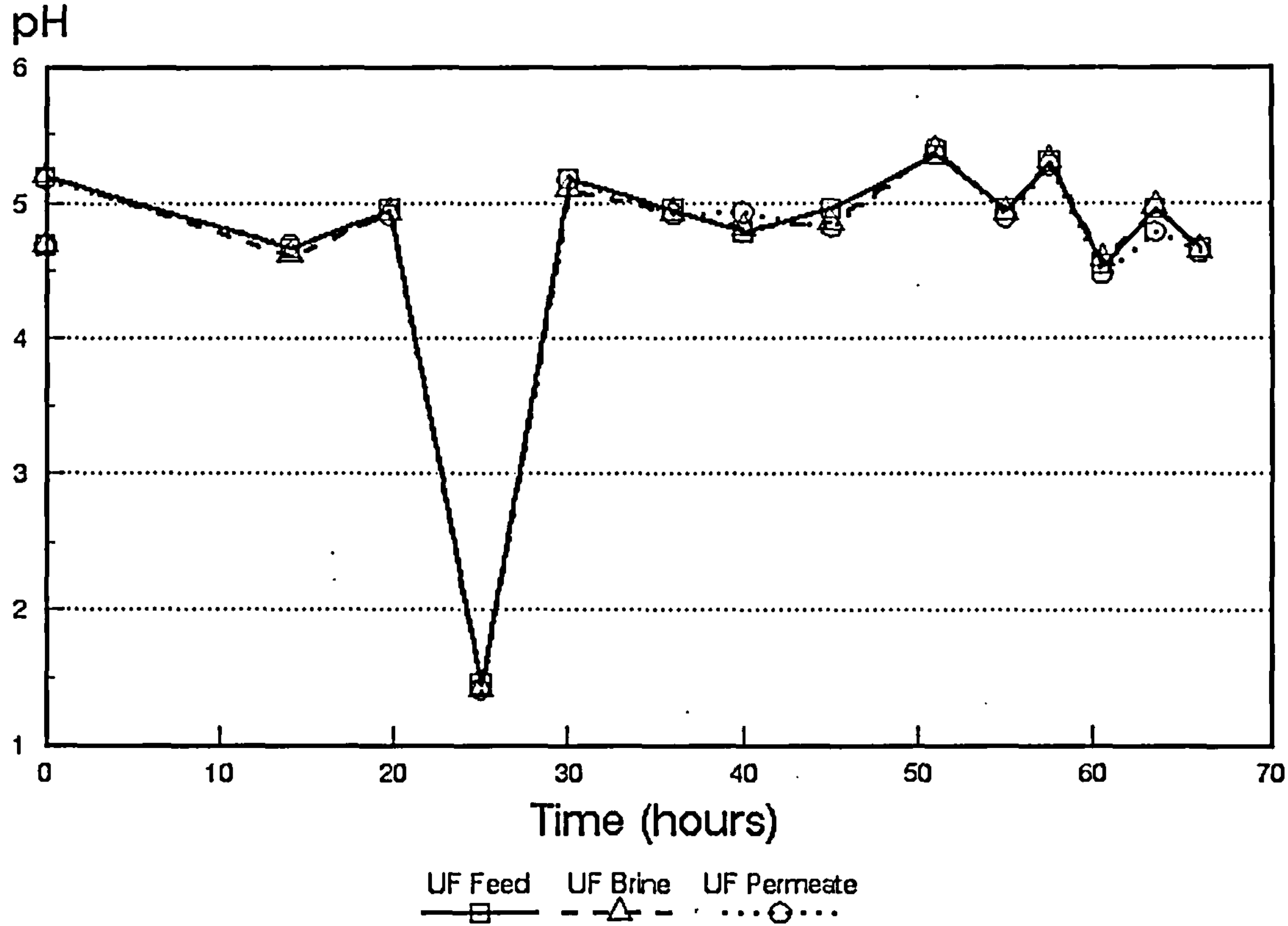

Figure 25 : pH of UF feed, brine and permeate as a function of time during UFRO treatment of the final effluent.

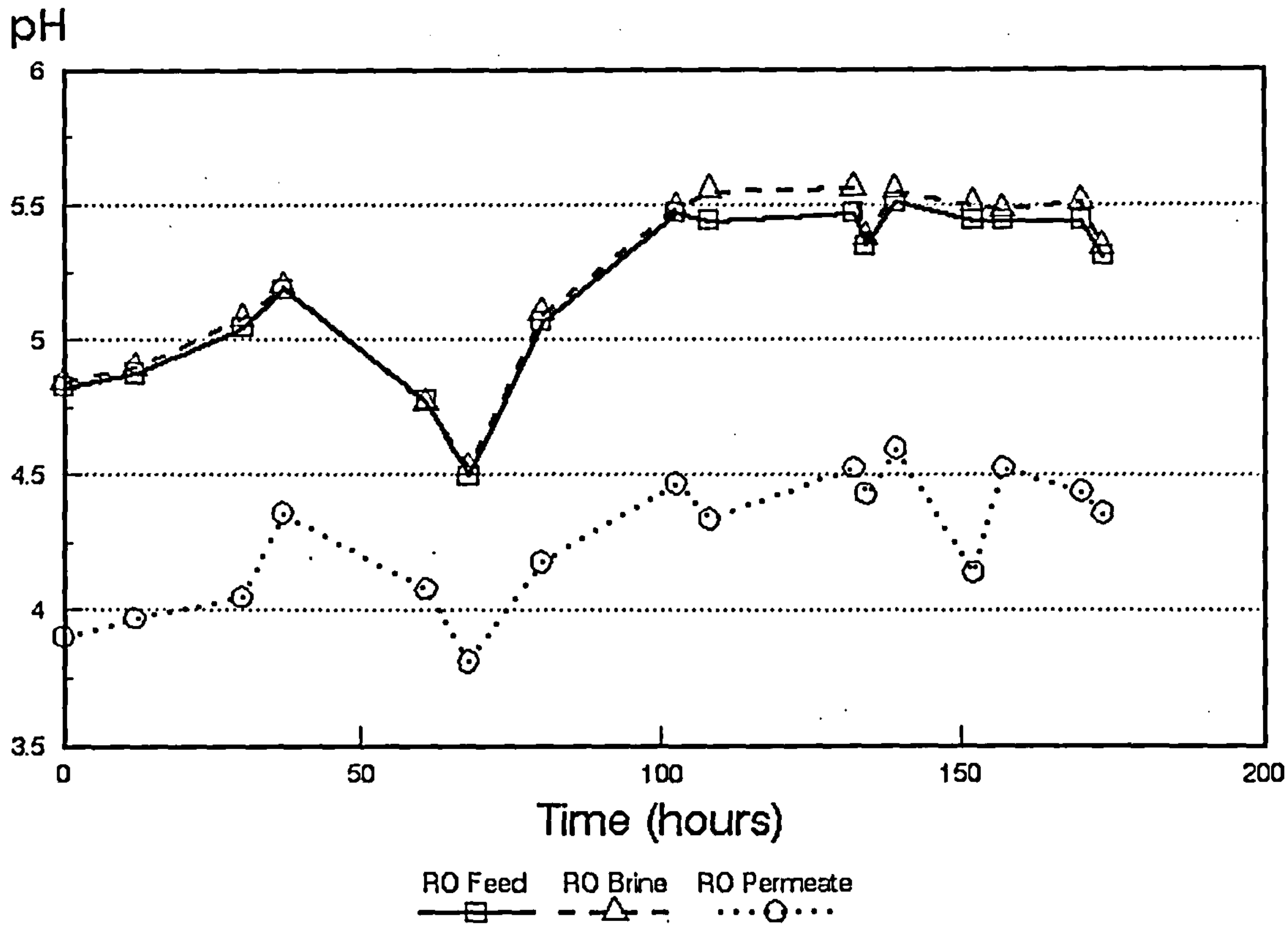

Figure 26 : pH of RO feed, brine and permeate as a function of time during UFRO treatment of the final effluent.

were 415 and 447 mg/ℓ (Tables 13 and 14). It is also interesting to note that almost no iron and manganese have been removed by UF. The iron and manganese are most probably complexed with organics in the effluent which passes unhindered through the UF membranes. Some sulphide, however, was removed with UF.

Table 13 : Chemical composition of UF feed, permeate and brine (after 12 hours of operation)

Constituents (mg/ℓ)	Feed	Permeate	Brine
Sodium	3 020	3 030	3 010
Potassium	84	80	83
Calcium	415	388	377
Magnesium	185,1	156	160
TKN as N	807,3	813,2	848,1
Ammonia as N	624,9	611,3	616,8
Nitrate as N	11,39	6,6	9,12
Sulphate	3 739	3 652	3 957
Chloride	3 700	3 188	4 831
Alkalinity as $CaCO_3$	300	275	295
COD	1 920	1 830	2 110
Sulphide	3,2	1,6	3,2
Chromium	0,5	0,4	0,5
Iron	216	207	198
Fluoride	3,4	3	3,6
Manganese	8	7,7	8
Fats and Oils	—	—	—
pH	5,19	5,17	5,2
Conductivity (mS/m)	1 790	1 770	1 800
TDS	12 985	12 771	—

Table 14 : Chemical composition of UF feed, permeate and brine (after 67,75 hours of operation)

Constituents (mg/ℓ)	Feed	Permeate	Brine
Sodium	2 890	2 770	2 820
Potassium	146	158	130
Calcium	447	469	442
Magnesium	149,1	161,3	148,5
TKN as N	582,6	573,5	583,9
Ammonia as N	503,3	509,2	514,4
Nitrate as N	4,48	2,01	4,16
Sulphate	2 400	1 782	1 927
Chloride	4 389	5 544	4 418
Alkalinity as $CaCO_3$	350	400	350
COD	2 260	2 140	2 270
Sulphide	—	—	—
Chromium	1,1	0,6	1,3
Iron	167	167	162
Fluoride	4,1	2,6	4,4
Manganese	9	8,6	8,9
Fats and Oils	11,7	< 5	11,5
pH	5,18	5,17	5,1
Conductivity (mS/m)	1 820	1 800	1 810
TDS	12 643	13 033	12 947

Table 15 : Chemical composition of RO feed, permeate and brine (after 12 hours of operation)

Constituents (mg/ℓ)	Feed	Permeate	Brine	Rejection %
Sodium	5 010	433	5 430	91,36
Potassium	144	17,3	153	87,99
Calcium	707	26,2	711	96,29
Magnesium	255	9,1	267	96,43
TKN as N	856,4	239,1	799,1	72,08
Ammonia as N	942,4	121,12	1 010	87,15
Nitrate as N	6,57	5,23	6,54	20,40
Sulphate	5 006	101	7 200	97,98
Chloride	7 262	1 009	5 226	86,11
Alkalinity as $CaCO_3$	175	0	200	100,00
COD	2 800	610	2 790	78,21
Sulphide	1,6	< 0,1	1,6	93,75
Chromium	1,3	0	1,2	100,00
Iron	393	9,5	392	97,58
Fluoride	4,8	0,3	4,1	93,75
Manganese	13,6	0,5	14,9	96,32
Fats and Oils	—	—	—	—
pH	4,88	3,97	4,9	—
Conductivity (mS/m)	2 880	363	2 980	87,40
TDS	23 167	1 465	23 441	93,68

Table 16: *Chemical composition of RO feed, permeate and brine (67,75 hours of operation)*

Constituents (mg/ℓ)	Feed	Permeate	Brine	Rejection %
Sodium	6 960	628	7 190	90,98
Potassium	277	24	360	91,34
Calcium	1 250	33,7	1 240	97,30
Magnesium	376	14,8	392	96,06
TKN as N	1 343	202,9	1378,8	84,89
Ammonia as N	1 100	183,9	1 130	83,28
Nitrate as N	3,79	3,09	4,82	18,47
Sulphate	10 037	135	—	98,66
Chloride	3 933	1 344	9 570	65,83
Alkalinity as $CaCO_3$	187,5	0	187,5	100,00
COD	3 990	1 090	4 090	72,68
Sulphide	—	—	—	—
Chromium	3,3	0,11	3,4	96,67
Iron	532	12,3	560	97,69
Fluoride	5,9	2,2	7,7	62,71
Manganese	20,7	0,43	20,9	97,92
Fats and Oils	< 5	< 5	< 5	—
pH	4,5	3,81	4,53	—
Conductivity (mS/m)	3 920	537	4 020	86,30
TDS	33 200	2 281	34 156	93,12

Electrical conductivity removals of 87 and 86,3 percent were obtained with RO (Tables 15 and 16). Electrical conductivity in the RO feed was in one case reduced from 2 880 mS/m to 363 mS/m in the permeate (Table 15). In another case, the electrical conductivity of the RO feed was reduced from 3 920 mS/m to 537 mS/m in the RO permeate (Table 16). Therefore, an excellent quality RO product water could be produced. It should be possible to discharge the RO permeate in the municipal treatment system or possible to reuse the RO permeate at the tannery.

Brine will comprise thirty percent of the RO feed at seventy percent water recovery. Typical brine concentration levels are shown in Tables 15 and 16. Brine electrical conductivity levels of 2 980 and 4 020 mS/m were obtained. The brine also contained high concentration levels of ammonia-nitrogen (1 010 and 1 130 mg/ℓ); chromium (1,2 and 3,4 mg/ℓ); fluoride 4,1 and 7,7 mg/ℓ; and COD (2 790 and 4 090 mg/ℓ). This brine should be disposed of safety so as not to pollute surface and groundwater sources.

7. CROSSFLOW MICROFILTRATION REVERSE OSMOSIS TREATMENT OF SOAK PADDLE EFFLUENT

Soak paddle effluent from the soak paddles as well as effluent from the sump containing effluent from the soak paddles, fleshing, splitting, deliming and certain stages of the tanning operations were treated with CFMFRO. Permeate from the CFMF unit was used as feed to the RO unit. Preliminary tests were also conducted to evaluate dissolved air flotation and coagulation / flocculation for suspended solids removal from the effluent.

7.1 *Effluent pretreatment*

7.1.1 *Dissolved air flotation of soak paddles effluent*

Dissolved air flotation (DAF) treatment of the effluent on laboratory scale with the addition of coagulant (150 mg/ℓ Al^{3+}) did not result in the flotation of suspended solids in the effluent. The suspended solids settled out. Therefore, it appeared that DAF would not function effectively for effluent clarification prior to RO desalination.

7.1.2 *Coagulation / flocculation of soak paddles effluent*

Coagulation / flocculation results with alum are shown in Table 17. Excellent turbidity removals were obtained. The turbidity of the effluent could be reduced by 88,6 and 96,6 percent with dosages of 100 and 150 mg/ℓ Al^{3+}, respectively. A COD removal of 71,7 percent was obtained with an Al^{3+} dosage of 150 mg/ℓ . Therefore, it appeared that alum coagulation / flocculation of the effluent should function effectively for removal of most of the suspended material and organics from the effluent prior to RO desalination.

Table 17 : Coagulation / flocculation of soak paddles effluent with alum

Alum Dosage mg/ℓ Al^{3+}	pH	Conductivity (mS/m)	COD		Turbidity*	
			mg/ℓ	% Removal	NTU	% Removal
0	7,96	7 260	12 000		1750	
50	7,15	7 250			275	84,3
100	7,07	7 270			200	88,6
150	7,02	7 300	34 000	71,67	60	96,6

*Turbidity measured after filtration through Whatmann No. 40 filter paper.

7.2 Cross flow microfiltration treatment of soak paddle effluent

Permeate flux varied between 319 and 222 ℓ/m².d and between 199 and 175 ℓ/m².d for two runs that were conducted[6]. The lower permeate flux that was obtained for the one run could be ascribed to membrane fouling. No attempt was made to clean the membranes. Water recoveries were 73,8 and 63 percent, respectively.

The COD and turbidity of the soak paddle effluent are shown in Table 18.

Table 18 : COD and turbidity of soak paddle effluent (run 1)

Constituent	Feed	Permeate	% Removal
COD (mg/ℓ)	12 000	6 730	43,9
Turbidity (NTU)	1 700	3,5	99,8

The COD and turbidity of the soak paddle effluent are high. Excellent turbidity removal was obtained (99,8% removal). COD removal, however, was not as good as only 43,9 percent of the organics was removed.

Another four batch runs were conducted by treating soak paddle effluent with CFMF[6]. The COD of the effluent in this case was lower than in the previous case (approximately 5 000 mg/ℓ). COD and turbidity removals for the runs are shown in Tables 19 and 20.

Table 19 : COD concentration of CFMF feed, product and brine (soak paddle effluent)

Batch No.	Feed COD mg/ℓ	Product COD mg/ℓ	Brine COD mg/ℓ	% Removal
1	4 590	1 170	8 050	74,5
2	4 750	1 380	8 090	71,0
3	5 440	2 100	9 120	61,4

Table 20 : Turbidity of CFMF feed, product and brine (soak paddle effluent)

Batch No.	Feed (mg/ℓ)	Permeate (mg/ℓ)	% Removal
1	1 350	12	99,1
2	840	24	97,1
3	1 340	23	98,3

COD removals varied between 61 and 74,5 percent for the three batches. Turbidity removals varied between 97,1 and 99,1 percent. Therefore, excellent turbidity removals were obtained. (Note : water recoveries for the three batches were 67,3; 53,3; and 71%, respectively).

Effluent from the sump (see Figure 3) was also treated with CFMF[6]. The COD and turbidity results are shown in Table 21.

Table 21 : COD and turbidity of the CFMF feed and product (sump effluent)

Constituent	Feed	Permeate	% Removal
COD (mg/ℓ)	4 300	3 720	13,5
Turbidity (NTU)	800	17	97,9

The COD and turbidity of the sump effluent could be reduced by 13,5 and 97,9 percent, respectively. However, poor COD removal was experienced in this case. Turbidity removal, however, was good.

7.3 Reverse osmosis treatment of soak paddle effluent

7.3.1 *Permeate flux as a function of time and percentage water recovery during treatment of a relatively concentrated soak paddle effluent.*

Soak paddle effluent with an electrical conductivity of 7 160 mS/m was batch wise treated with RO. Permeate flux as a function of time and percentage water recovery is shown in Figures 27 and 28, respectively. The RO permeate flux varied between 87 and 20 $\ell/m^2.d$. The average flux was calculated as 75,5 $\ell/m^2.d$. The low permeate flux that was experienced could be ascribed to the high electrical conductivity of the RO feedwater.

The CWF at the start of the run was 608 $\ell/m^2.d$ and decreased to 586 $\ell/m^2.d$ at the end of the run. Cleaning of the membranes with citric acid increased the CWF to 613 $\ell/m^2.d$. Therefore, it appeared that it should be possible to control membrane fouling with chemical cleaning. However, many more runs should be conducted to prove this point.

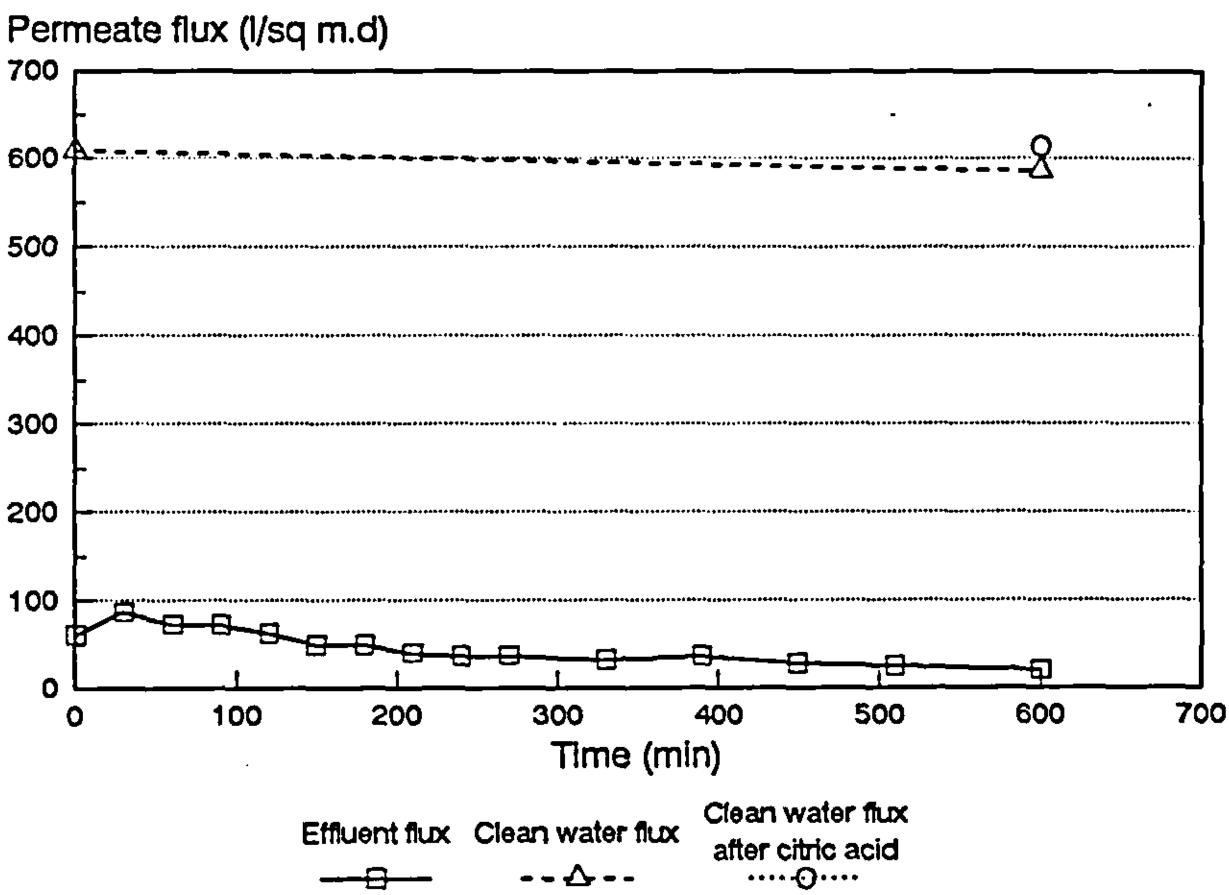

Figure 27 : Permeate flux as a function of time during treatment of soak paddle effluent with RO.

Water recovery was 69,4 percent when the run was terminated (Figure 28).

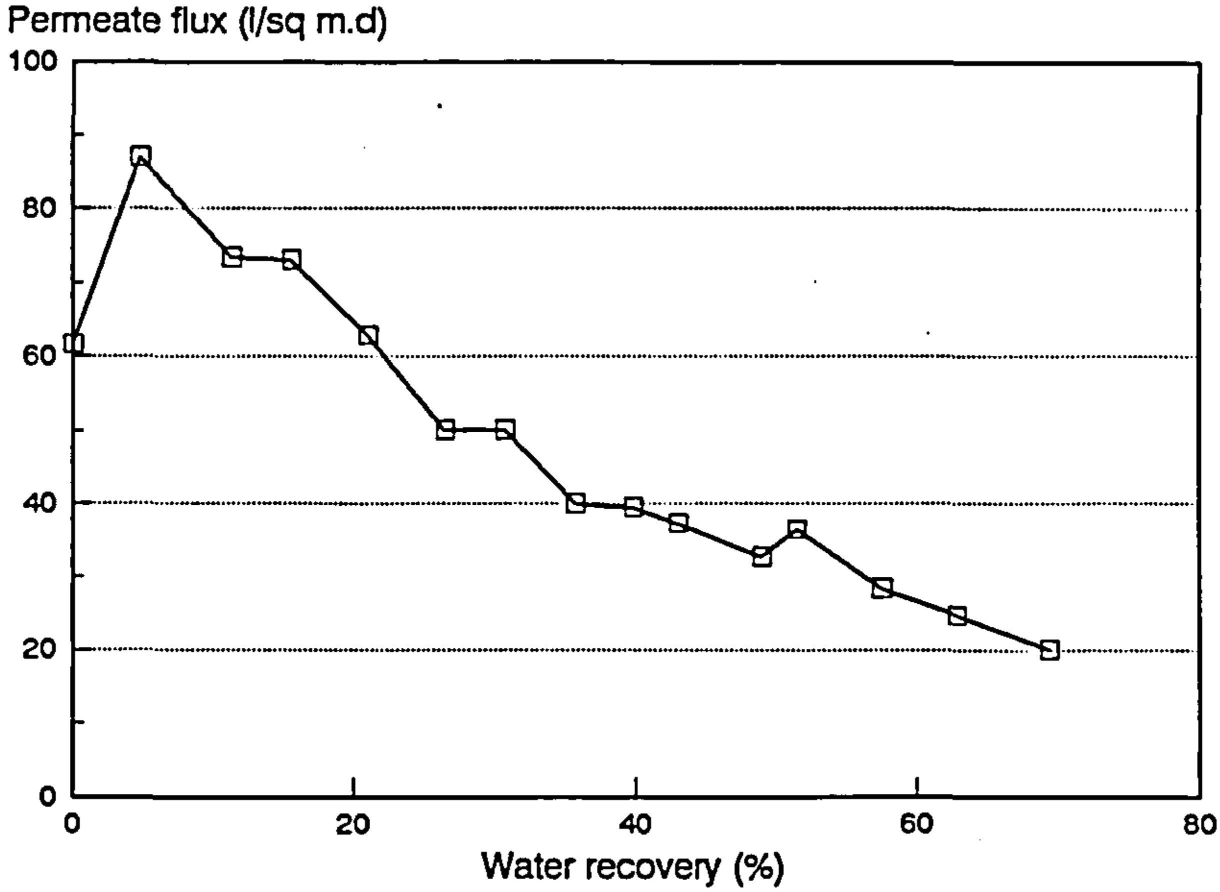

Figure 28 : Permeate flux as a function of water recovery during treatment of soak paddle effluent with RO.

7.3.2 *Electrical conductivity and COD of RO feed, permeate and brine*

The electrical conductivity, TDS and COD of the RO feed, permeate and brine are shown in Table 22. Electrical conductivity removal as a function of percentage recovery is shown in Figure 29.

Table 22 : Electrical conductivity, TDS and COD of RO feed, permeate and brine

Constituent	Feed	Permeate	Brine	% Removal
Conductivity (mS/m)	7 160	3 730	10 780	46,5
TDS (mg/ℓ)	47 080	23 100	83 650	50,9
COD (mg/ℓ)	2 790	890	5 830	68,1

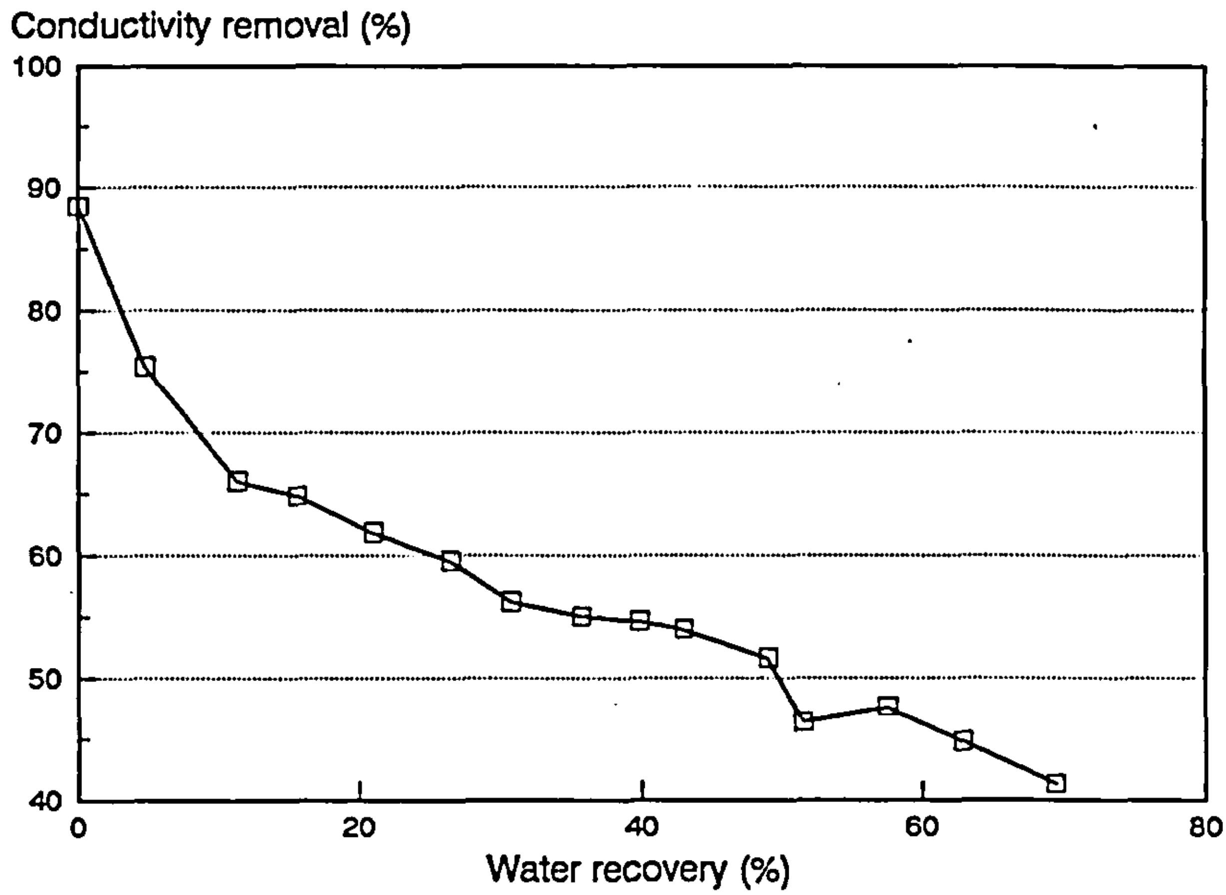

Figure 29 : Electrical conductivity removal as a function of water recovery during treatment of the soak paddle effluent (cellulose acetate RO membranes)

Poor electrical conductivity removal was obtained. Conductivity removal was only 46,5 percent at the end of the run. This poor conductivity removal could be ascribed to fouled membranes and/or high salt passage through the membranes at the high feed concentration that was used for the RO run. A COD removal of 68,1 was obtained.

The electrical conductivity removal versus percentage water recovery graph shows how the conductivity removal decreases with increasing water recovery. The electrical conductivity decrease can be ascribed to an increasing salt passage through the membranes with increasing water recovery.

Brine volume comprised approximately 30 percent of the treated feed. The electrical conductivity and COD of the RO brine are high. This brine should be disposed of safely.

The electrical conductivity of the RO permeate was still high. However, a significant amount of salinity could be removed from the soak paddle effluent with RO. The electrical conductivity of a very concentrated soak paddle effluent is probably too high for the successful treatment of soak paddle effluent with RO.

7.3.3 *Reverse osmosis treatment of a relatively less concentrated soak paddle effluent*

Less concentrated soak paddle effluent with electrical conductivities of less than 3 500 mS/m was also treated (batch wise) with RO. Reverse osmosis permeate flux as a function of time and percentage water recovery is shown in Figures 30 and 31. Permeate flux decreased as a function of time and percentage water recovery for the four batch runs. The initial conductivity for the first run was 2 580 mS/m and that of the second and third runs 2 710 and 2 700 mS/m, respectively. The initial feed conductivity for the fourth run was 3 430 mS/m. This higher initial conductivity explained the lower permeate flux that was obtained.

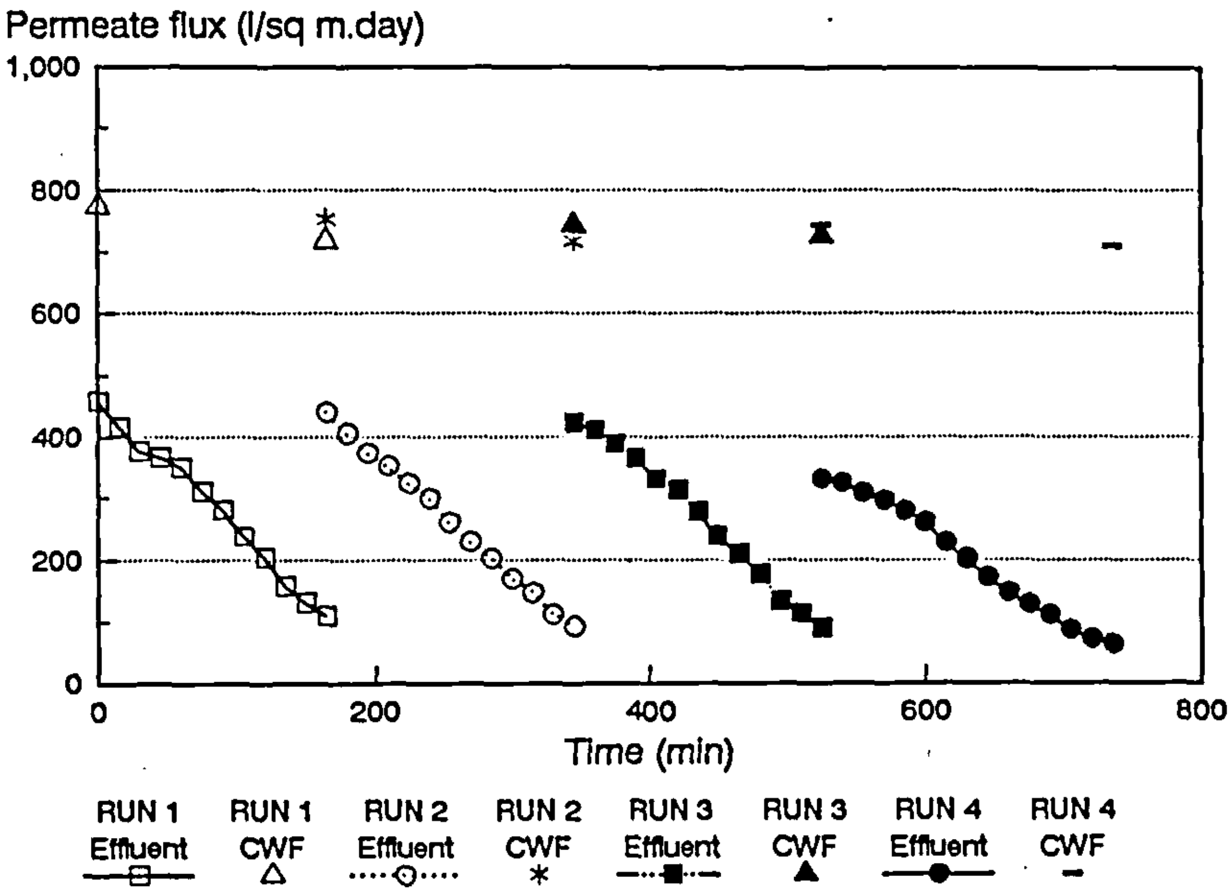

Figure 30 : Permeate flux as a function of time during treatment of the soak paddle effluent with RO (cellulose acetate RO membranes)

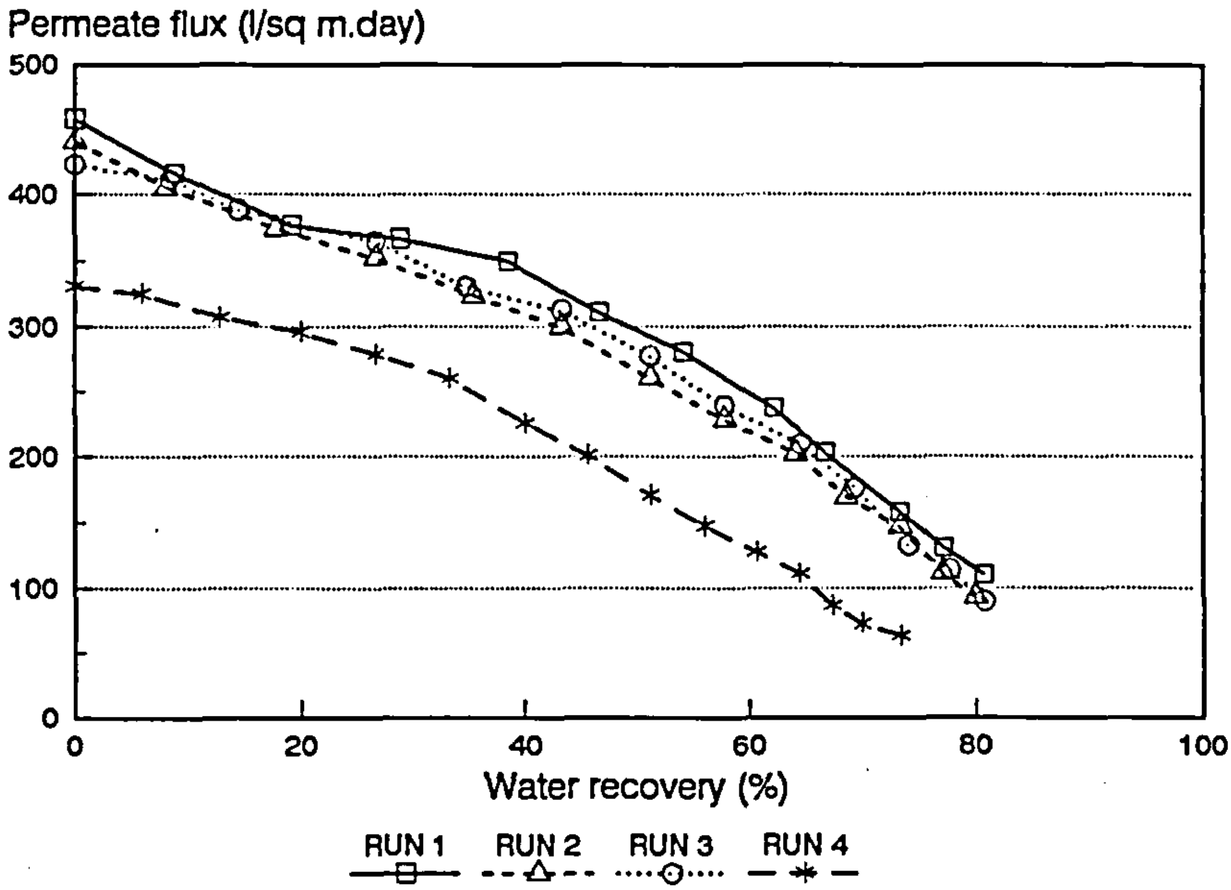

Figure 31 : Permeate flux as a function of water recovery during treatment of soak paddle effluent with RO.

The CWF at the start of the run was 773 ℓ/m^2.d. Clean water flux decreased to approximately 717 ℓ/m^2.d after the first run. Clean water flux, however, increased to approximately 752 ℓ/m^2.d after the membranes were preserved in 0,25 percent sodium metabisulfite solution. The CWF after the second run was 717 ℓ/m^2.d and increased to 743 ℓ/m^2.d after membrane preservation as before. Clean water flux after the third run was 726 ℓ/m^2.d and increased to 743 ℓ/m^2.d after membrane preservation. Clean water flux after the fourth run was 708 ℓ/m^2.d. Therefore, a decline in the CWF of the membranes was experienced (from 773 ℓ/m^2.d to 708 ℓ/m^2.d before membrane preserv-ation). This showed that membrane fouling was experienced despite the fact that microfiltered effluent was used as feed to the RO unit. Membrane fouling, however, did not appear to be severe. No chemical membrane cleaning was also applied.

The average permeate fluxes for the four runs were 224,9; 207,8; 200 and 151,7 ℓ/m^2.d, respectively. These average flux values can be used for membrane plant design purposes.

Water recoveries of approximately 80% were obtained for the first three runs while water recovery was only approximately 70% for run 4. The fourth run was terminated because a very low permeate flux was experienced towards the end of the run.

7.3.4 *Chemical composition of RO feed, permeate and brine.*

The chemical composition of the RO feed, permeate and brine for the four batch runs is shown in Tables 23 to 26. Electrical conductivity removal for the four runs varied between approximately 81 and 82 percent. Feed conductivity was reduced from 2 580 mS/m to 456 mS/m for run 1; from 2 710 mS/m to 513 mS/m for run 2; from 2 700 mS/m to 509 mS/m for run 3; and from 3 430 mS/m to 598 mS/m for run 4. Therefore; it appears that an RO permeate electrical conductivity of approximately 500 mS/m can be obtained except in the case of the fourth run. However, higher rejection RO membranes will be able to produce RO permeate conductivities of less than 500 mS/m.

Table 23 : Chemical composition of the RO feed permeate and brine (Run 1)

Constituents	RO Feed	RO permeate	RO Brine	Rejection %
pH	5.96	5.72	6.98	
Conductivity (mS/m)	2 580	456	6 900	82.33
COD	960	180	5 310	81.25
Ammonia as N	80.73	23.87	188.15	70.43
Nitrate as N	0.05	0.04	0.04	20.00
Chloride	7 715	1 235.5	20 555	83.99
Fluoride	2.8	0.17	8.2	93.93
Alkalinity as $CaCO_3$	190	49	531	74.21
Sulphate	440	21	1 700	95.23
TDS	16 828	2 352	47 968	86.02
Iron	0.82	0.07	3.04	91.46
Potassium	62	11.7	162	81.13
Sodium	4 970	834	14 450	83.22
Magnesium	19.6	1.92	66.9	90.20
Calcium	53.8	24.6	173	54.28
Hardness as $CaCO_3$	215.03	69.33	707.41	67.76

Table 24 : Chemical composition of the RO feed, permeate and brine (Run 2)

Constituents	RO Feed	RO permeate	RO Brine	Rejection %
pH	6.04	5.65	7.38	
Conductivity (mS/m)	2 710	513	7 190	81.07
COD	1 070	141	4 420	86.82
Ammonia as N	77.98	24.2	181.5	68.97
Nitrate as N	0.04	0.04	0.03	0.00
Chloride	7 714	1 275	20 705	83.47
Fluoride	3.2	0.14	8.8	95.63
Alkalinity as $CaCO_3$	386	27.5	1 062	92.88
Sulphate	350	18	1 400	94.86
TDS	17 700	2596	49 120	85.33
Iron	0.77	0.02	2.05	97.40
Potassium	61	13.1	163	78.52
Sodium	5 250	843	14 210	83.94
Magnesium	20.2	1.41	71.5	93.02
Calcium	55.4	3.80	203	93.14
Hardness as $CaCO_3$	221.5	15.29	801.26	93.10

Table 25 : Chemical composition of the RO feed, permeate and brine (Run 3)

Constituents	RO Feed	RO permeate	RO Brine	Rejection %
pH	5.79	5.51	7.46	
Conductivity (mS/m)	2 700	509	7 010	81.15
COD	1 070	125	3 160	88.32
Ammonia as N	77.98	21.18	165	72.84
Nitrate as N	0.04	0.30	0.03	—
Chloride	7 714	1 286	21 225	83.33
Fluoride	3.2	0.14	9.9	95.63
Alkalinity as $CaCO_3$	386	26.5	886	93.13
Sulphate	350	18	1 400	94.86
TDS	17 700	2 852	47 796	83.89
Iron	0.77	0.03	2	96.10
Potassium	61	13.2	152	78.36
Sodium	5 250	880	13 630	83.24
Magnesium	20.2	1.54	67.1	92.38
Calcium	55.4	4.05	217	92.69
Hardness as $CaCO_3$	221.5	16.45	818	92.57

Table 26 : Chemical composition of the RO feed permeate and brine (Run 4)

Constituents	RO Feed	RO permeate	RO Brine	Rejection %
pH	6.12	5.44	7.84	
Conductivity (mS/m)	3 430	598	7 260	82.57
COD	2 025	140	4 965	93.09
Ammonia as N	42.36	14.58	74.49	65.58
Nitrate as N	0.02	0.04	0	-100.00
Chloride	7 524	1 420	19 080	81.13
Fluoride	2.9	0.18	4.5	93.79
Alkalinity as $CaCO_3$	406	21	412	94.83
Sulphate	710	69	2 000	90.28
TDS	22 664	3 152	51 708	86.09
Iron	0.83	0.24	2.20	71.08
Potassium	99	19.6	219	80.20
Sodium	7 250	1 056	16 220	85.43
Magnesium	28.1	1.44	61	94.88
Calcium	52.9	4.35	96.7	91.78
Hardness as $CaCO_3$	247.8	16.8	492.6	93.22

Ammonia nitrogen removals varied between 66 and 73 percent for the four runs that were conducted. The ammonia-nitrogen concentration levels in the RO permeate varied between 16 and 24 mg/ℓ. This level of ammonia-nitrogen in the RO permeate should be suitable for discharge into the municipal treatment system.

COD removals varied between 81 and 93 percent. The COD in the RO permeate varied between 125 and 180 mg/ℓ. Therefore, excellent COD removals were obtained.

Brine volume comprised between 70 and 80 percent of the RO feed. The electrical conductivity of the RO brine is high. Electrical conductivity varied between 6 900 and 7 260 mS/m. The ammonia-nitrogen levels varied between 74 and 181 mg/ℓ. COD in the brine varied between 3 160 and 5 310 mg/ℓ. Therefore, the brine should be disposed of safely.

7.4 Reverse osmosis treatment of sump effluent containing effluent from soak paddles, fleshing, liming, deliming and certain stages of the tanning operations

7.4.1 *Permeate flux as a function of time and percentage water recovery.*

Sump effluent was treated batch wise with RO. Permeate flux as a function of time and percentage wager recovery is shown in *Figures 32 and 33. The permeate flux started at* 519 ℓ/m^2.d and was determined at 238 $^2\ell$/m .d when the run was terminated at 87,5 percent water recovery. The average permeate flux was calculated as 330,5 ℓ/m^2.d.

The CWF before the run was started was 613 ℓ/m^2.d and was determined at 615 ℓ/m^2.d after the run was completed. Therefore, it appeared that no severe membrane fouling was taking place. This was expected because microfiltered effluent was used as feed for the RO batch run.

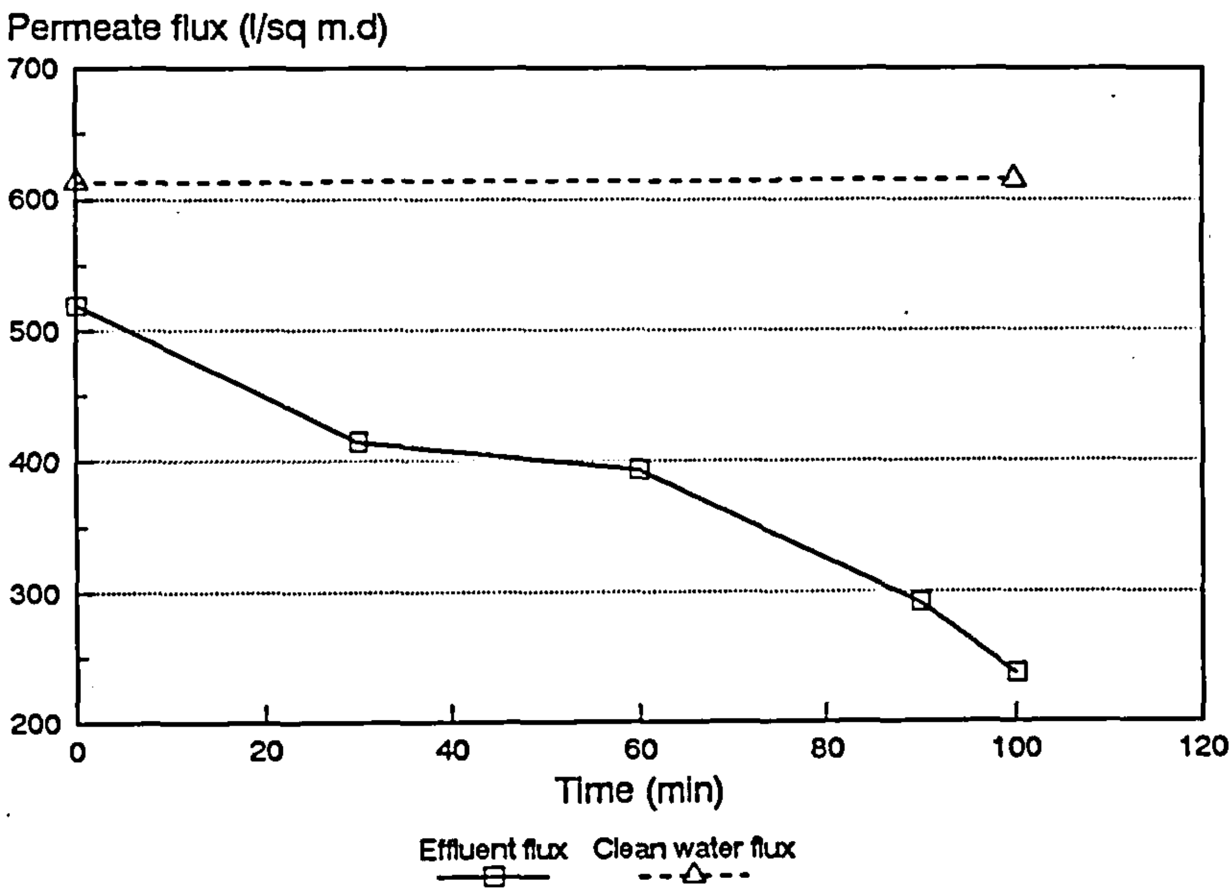

Figure 32 : Permeate flux as a function of time during treatment of the sump effluent with RO (cellulose acetate RO membranes)

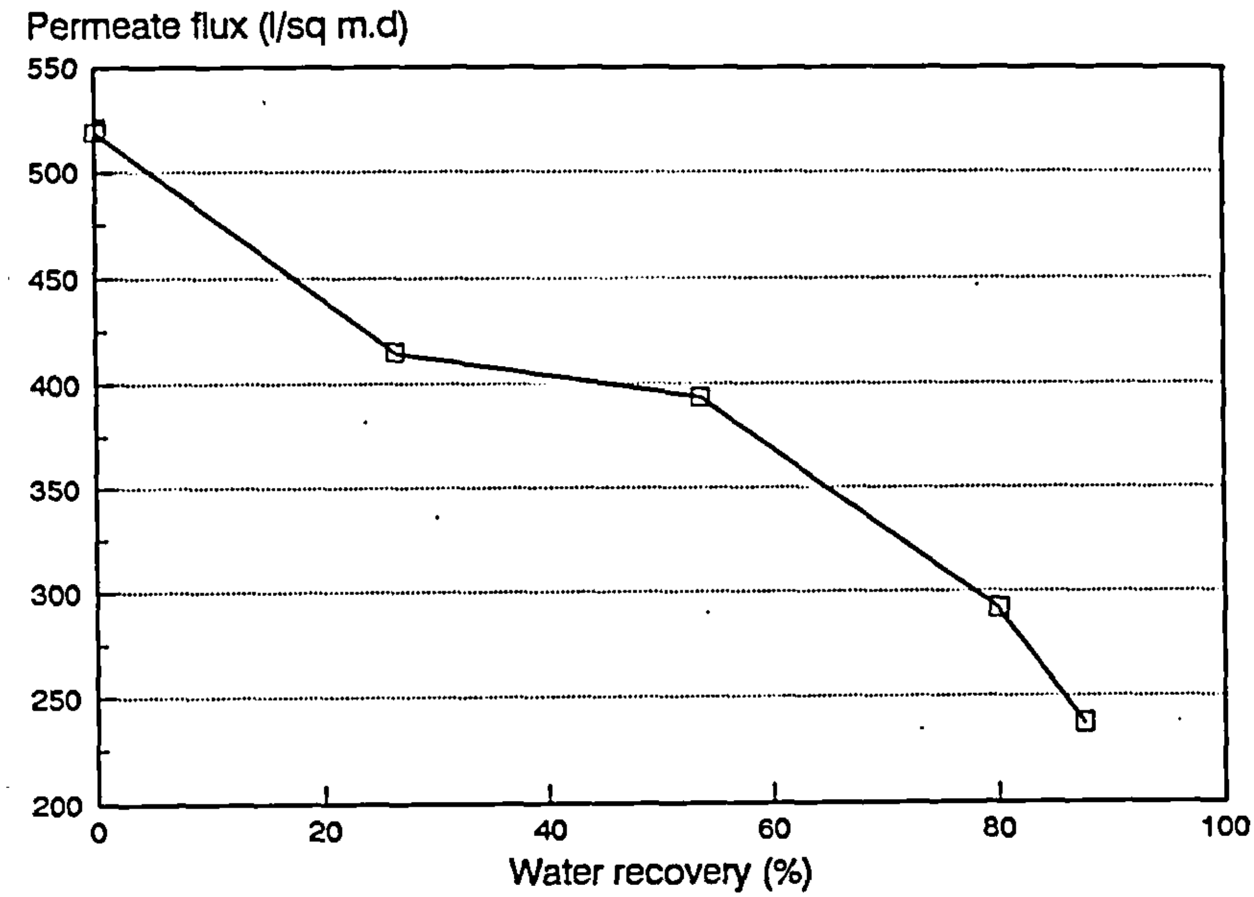

Figure 33 : Permeate flux as a function of water recovery during treatment of the sump effluent with RO (cellulose acetate RO membranes).

7.4.2 *Electrical conductivity and COD of RO feed, permeate and brine*

The electrical conductivity and COD of the RO feed, permeate and brine are shown in Table 27.

Table 27 : Electrical conductivity and COD of RO feed, permeate and brine

Constituent	Feed	Permeate	Brine	% Removal
Conductivity (mS/m)	1 104	128	3 620	88,4
TDS (mg/ℓ)	7 588	682	58 900	91,0
COD (mg/ℓ)	3 720	90	4 330	97,6

Electrical conductivity and COD removals were good. Electrical conductivity and COD removals were 88,1, and 97,6 percent, respectively. A satisfactory quality permeate could also be produced with RO. Water of this quality may be reused at a tannery. Brine volume comprised only 12,5 percent of the treated water. The electrical conductivity, however, of the brine is high. The brine should be disposed of safely.

8. ULTRAFILTRATION REVERSE OSMOSIS TREATMENT OF DYE-HOUSE EFFLUENT

8.1 Ultrafiltration treatment of dye-house effluent

Permeate flux as a function of time for the first run (flow reversal without sponge ball cleaning) is shown in Figure 34. Permeate flux rapidly declined (from 493,7 to 65,8 $\ell/m^2.d$) within the first 30 minutes of operation. The flux then remained approximately constant at 48 $\ell/m^2.d$ for the remainder of the run.

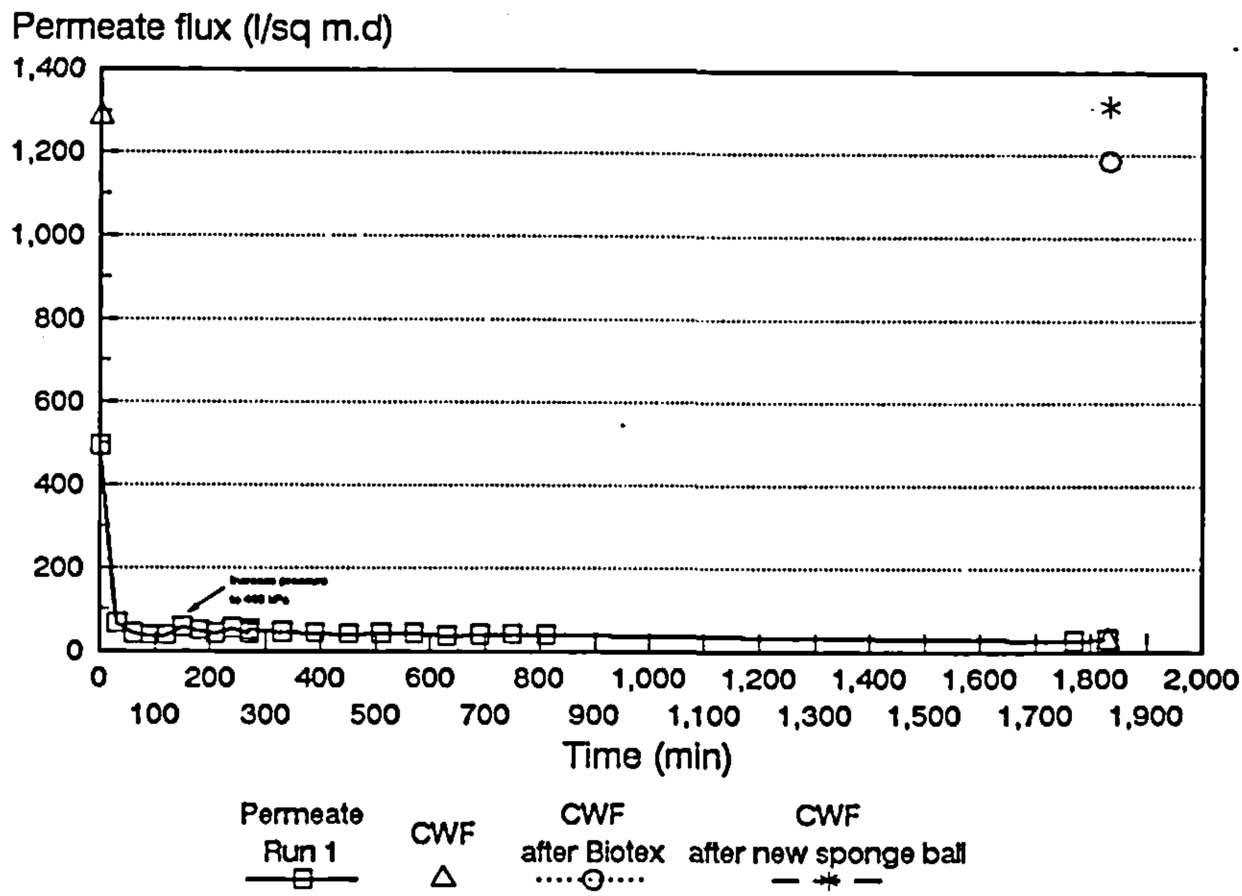

Figure 34 : Permeate flux as a function of time during treatment of dye-house effluent with UF (run 1; polysulphone UF membranes).

Feed pressure was increased after 120 minutes of operation from 200 to 400 kPa to determine whether a higher feed pressure would increase permeate flux. However, increase in feed pressure had almost no effect on permeate flux.

The CWF was determined at 1 248 ℓ/m².d in the beginning of the run. However, CWF decreased to 24 ℓ/m².d at the end of the run due to membrane fouling. Cleaning of the membranes with a 1 percent Biotex solution increased CWF to approximately 1 176 ℓ/m².d. Therefore, CWF could almost be restored. A sponge ball was inserted and the membranes were rinsed with tapwater for 30 minutes with flow reversal every 5 minutes. This resulted in a further increase in the CWF to approximately 1 318 ℓ/m².d. Therefore, it appeared that the CWF could be restored after cleaning of the membranes. This also demonstrated the cleaning effect of sponge balls on fouled membranes.

A second run was conducted but with sponge ball cleaning in this case (Figure 35).

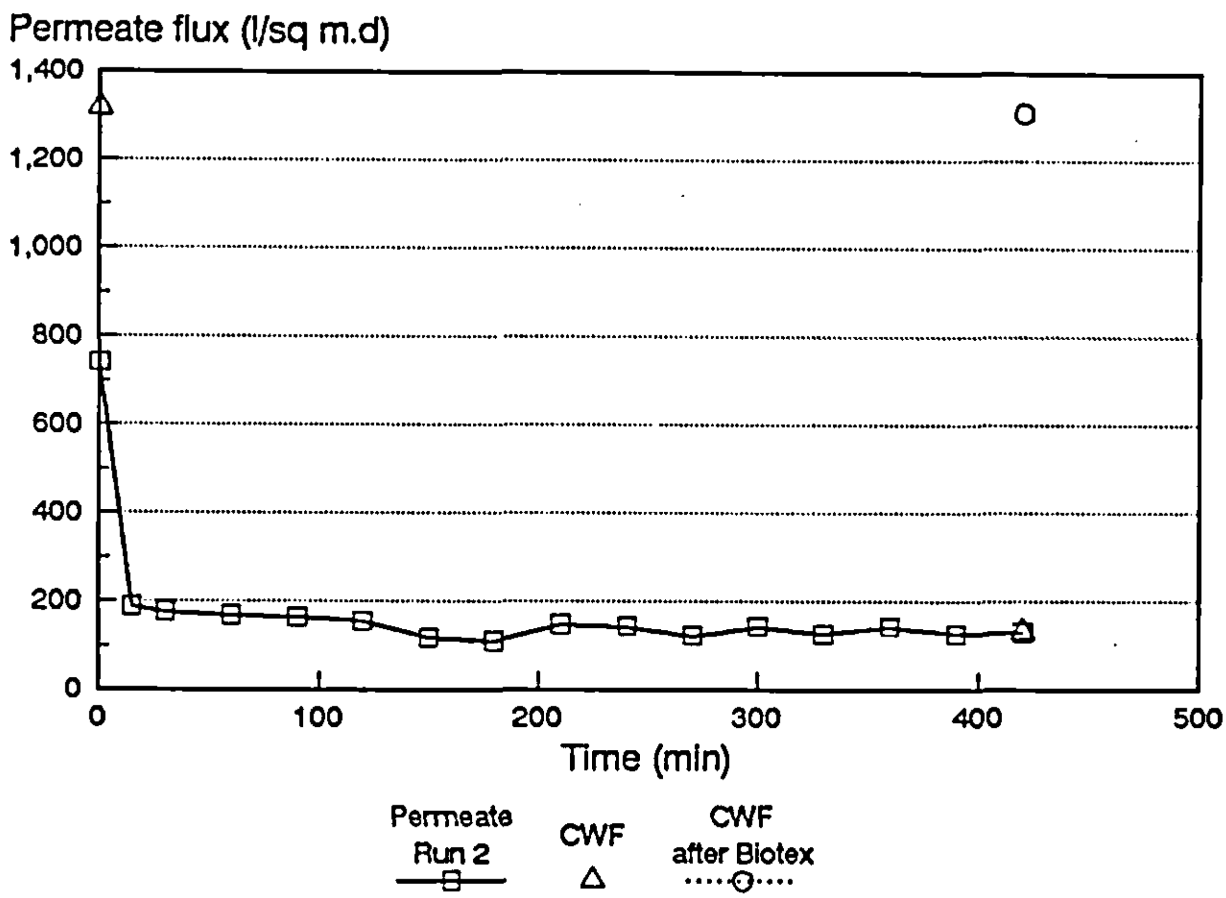

Figure 35 : Permeate flux as a function of time during treatment of dye-house effluent with UF (run 2; polysulphone UF membranes).

Permeate flux again rapidly declined from 741,6 ℓ/m^2.d in the beginning of the run to 189,6 ℓ/m^2.d after 15 minutes of operation. Permeate flux then steadily declined, remained more or less constant (approximately 144 ℓ/m^2.d) and was determined at 132 ℓ/m^2.d at the end of the run. This flux was significantly higher than the flux that was obtained during the first run.

The CWF was determined at 1 318 ℓ/m^2.d before the run was started and declined to 132 ℓ/m^2.d at the end of the run. Cleaning of the membranes with a 1 percent Biotex solution restored the CWF to 1 300 ℓ/m^2.d. Therefore, it appeared that the membranes could be successfully cleaned.

Permeate flux as a function of percentage water recovery for the two runs is shown in Figure 36. Water recoveries of approximately 90 percent were obtained for both runs.

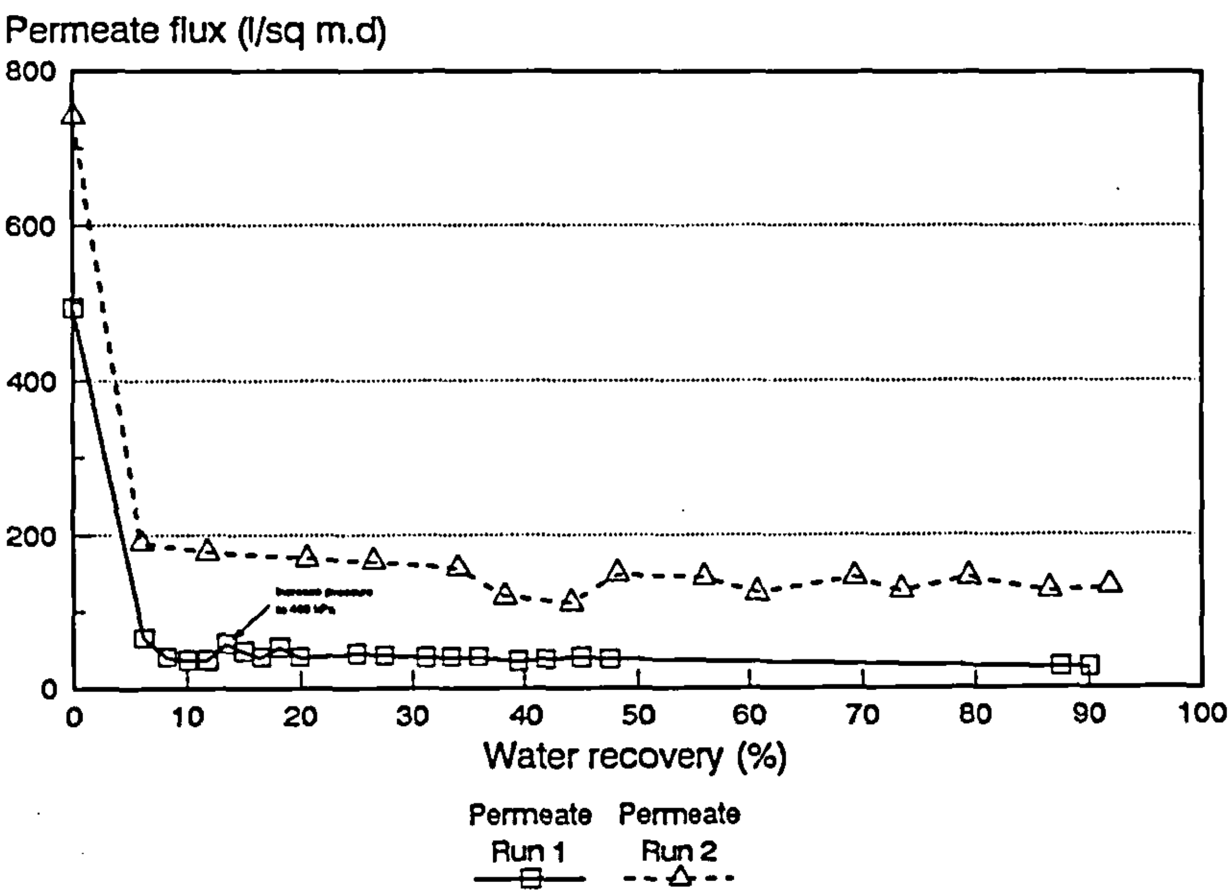

Figure 36 : Permeate flux as a function of water recovery during treatment of dyehouse effluent with UF (runs 1 and 2; polysulphone UF membranes).

8.2 Chemical composition of UF feed, product and brine

The chemical composition of the UF feed, permeate and brine is shown in Table 28.

Table 28 : Chemical composition of UF feed, product and brine (dye-house effluent)

Constituents	Dye-house effluent		
	Feed	Perm	Brine
pH	4,78	—	—
Conductivity (mS/m)	1 420	1 221	1 307
COD	22 900	7 440	79 000
Ammonia-N	728,3		
Nitrate-N	10,09		
Chloride	719,9		
Alkalinity	236,5		
Sulphate	5 100		
Suspended solids	220		
TDS	19 332		
Chromium	21,1		
Chromium (VI)	10		
Iron	4,5		
Potassium	85		
Sodium	2 057		
Magnesium	74,6		
Calcium	87,5		

The electrical conductivity (1 420 mS/m), COD (22 900 mg/ℓ), ammonia-nitrogen (728,3 mg/ℓ), sulphate (5 100 mg/ℓ), chromium (21,1 mg/ℓ total) and sodium (2 057 mg/ℓ) concentration levels of the effluent are high. The chromium (vi) concentration level was determined at 10 mg/ℓ . COD removal was 67,5 percent.

8.3 Reverse osmosis treatment of dye-house effluent

Permeate flux as a function of time and percentage water recovery is shown in Figures

37 and 38. Permeate flux was 444,8 ℓ/m².d in the beginning of the batch run and declined to 187,2 ℓ/m².d at the end of the run. The average permeate flux was determined as 272 ℓ/m².d.

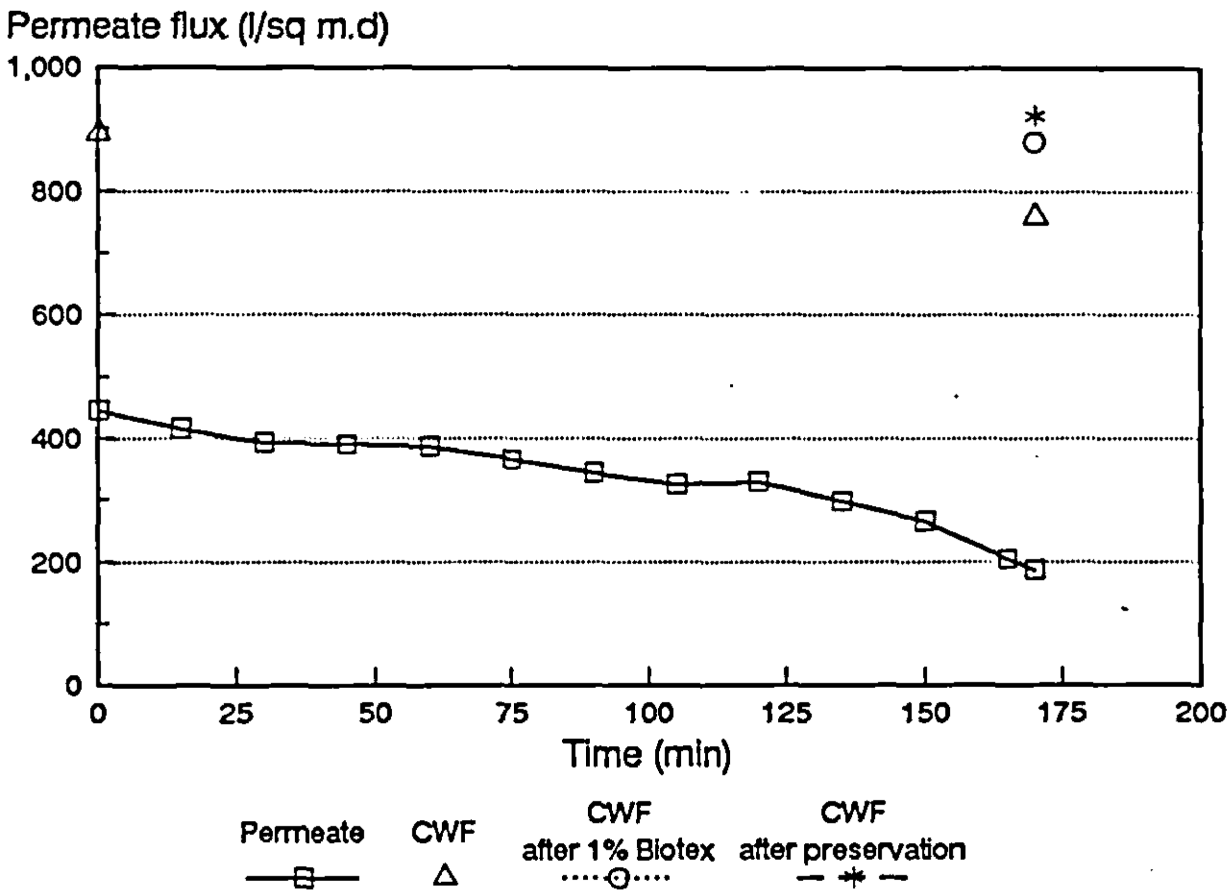

Figure 37 : Permeate flux as a function of time during RO treatment of dye-house effluent (cellulose acetate RO membranes)

The initial CWF was 894, ℓ/m².d and CWF declined to 758,2 ℓ/m².d at the end of the run. Therefore, membrane fouling was taking place. Cleaning of the membranes with a 1 percent Biotex solution increased CWF to 879,8 ℓ/m².d. Clean water flux further improved to 923,3 ℓ/m².d after preservation of the membranes in 0,25 percent sodium metabisulfite solution. Therefore, it appeared that CWF could be restored.

A water recovery of approximately 80 percent was obtained (Figure 38).

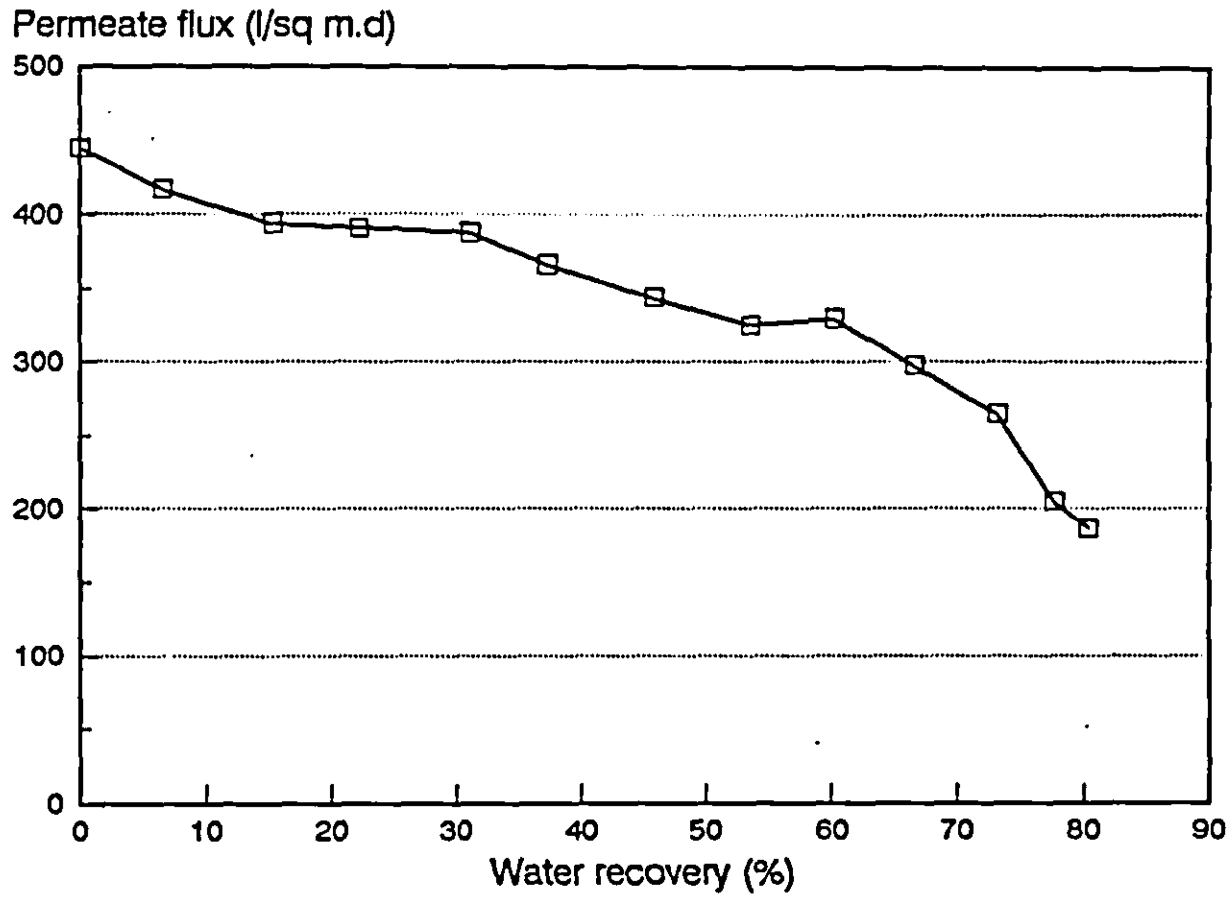

Figure 38 : Permeate flux as a function of percentage water recovery during treatment of dye-house effluent (cellulose acetate RO membranes)

8.4 Chemical composition of RO feed, permeate and brine

The chemical composition of the RO feed, permeate and brine is shown in Table 29. The feed electrical conductivity could be reduced from 1 181 mS/m to 156 mS/m (86,8% removal). Ammonia-nitrogen was removed from 456,1 to 64,2 mg/ℓ (85,9% removal). Very good chromium (vi) removals could be obtained with RO desalination. Chromium (vi) could be reduced from 0,9 mg/ℓ in the RO permeate to 0,05 mg/ℓ in the RO permeate. Generally speaking, a good quality permeate could be produced with RO treatment of the dye-house effluent. Reuse-use of this quality permeate should be investigated at a tannery.

Brine comprises approximately 80 percent of the treated feed. This brine contains toxic chromium (vi) (2,0 mg/ℓ) and high concentration levels of ammonia-nitrogen (1 494 mg/ℓ) and TDS (48 828 mg/ℓ) and should be disposed of safely.

Table 29 : Chemical composition of RO feed, permeate and brine (Dye-house effluent)

Constituents	Dye-house effluent			Rejection (%)
	Feed	Permeate	Brine	
pH	4,47	3,75	4,91	
Conductivity (mS/m)	1 181	156	3 480	86,79
COD	6 710	963	21 100	85,65
Ammonia-N	456,1	64,2	1 494	85,92
Nitrate-N	0,66	0,28	0,49	57,58
Chloride	814,4	85,54	3 072	89,50
Alkalinity	347	—	1 118,5	100,00
Sulphate	2 300	52	9 500	97,74
TDS	11 060	776	46 828	92,98
Chromium	8,4	0,4	33,1	95,24
Chromium (VI)	0,9	0,05	2,0	94,44
Iron	3,7	0,08	10,7	97,84
Potassium	70	8,2	289	88,29
Sodium	1 733	179,9	5 660	89,62
Magnesium	41,4	1,64	228	96,04
Calcium	106	8,7	295	91,79

9. ULTRAFILTRATION REVERSE OSMOSIS TREATMENT OF LIMING AND DELIMING EFFLUENT

9.1 Ultrafiltration treatment of liming effluent

Permeate flux as a function of time during UF treatment of the liming effluent is shown in Figure 39. Permeate flux declined rapidly in the beginning of the run from 616 ℓ/m^2.d to 316,8 ℓ/m^2.d after 30 minutes of operation. Permeate flux then declined steadily and was determined at 242,6 ℓ/m^2.d when the run was terminated.

Clean water flux declined from 1 111 ℓ/m^2.d before the run to 120 ℓ/m^2.d at the end of the run. Clean water flux was 1 135 ℓ/m^2.d after the membranes were cleaned with a 1 percent Biotex solution. Therefore, CWF could be restored.

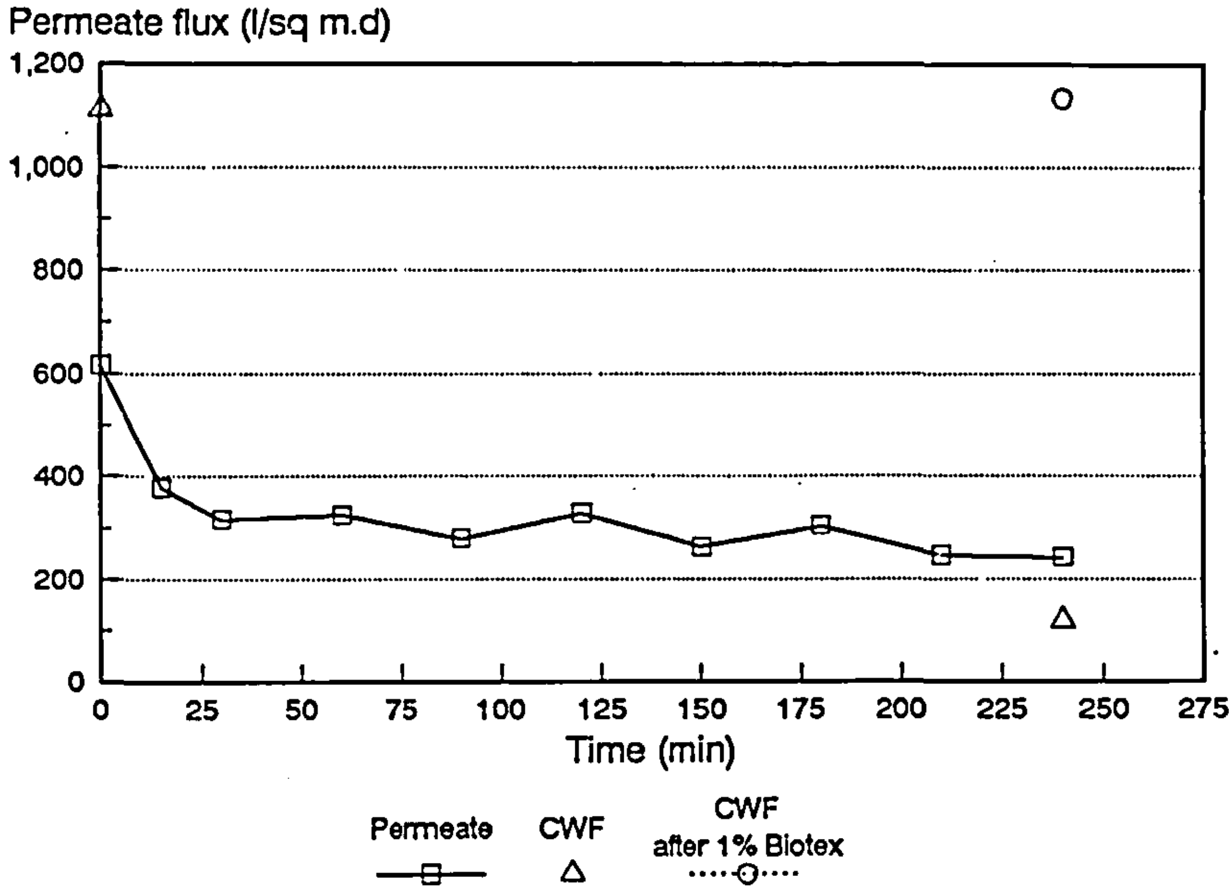

Figure 39 : Permeate flux as a function of time during UF treatment of the liming effluent (polysulphone UF membranes).

Permeate flux as a function of time during UF treatment of the deliming effluent is shown in Figure 40. Permeate flux declined rapidly in the beginning of the run from 552 $\ell/m^2.d$ to 384 $\ell/m^2.d$ after 15 minutes of operation and then steadily declined to 240 $\ell/m^2.d$ at the end of the run.

The CWF was 1 135 $\ell/m^2.d$ before the run was started and was determined at 478 $\ell/m^2.d$ at the end of the run. Cleaning of the membranes with 1 percent Biotex solution improved the CWF to 773 $\ell/m^2.d$. Therefore, CWF flux could not be restored to its initial value with a Biotex cleaning in this case. However, CWF could be further increased to 936 $\ell/m^2.d$ after preservation of the membranes in 0,25 percent sodium metabisulfite solution. It seems, however, that it should be possible to restore CWF with subsequent membrane cleanings.

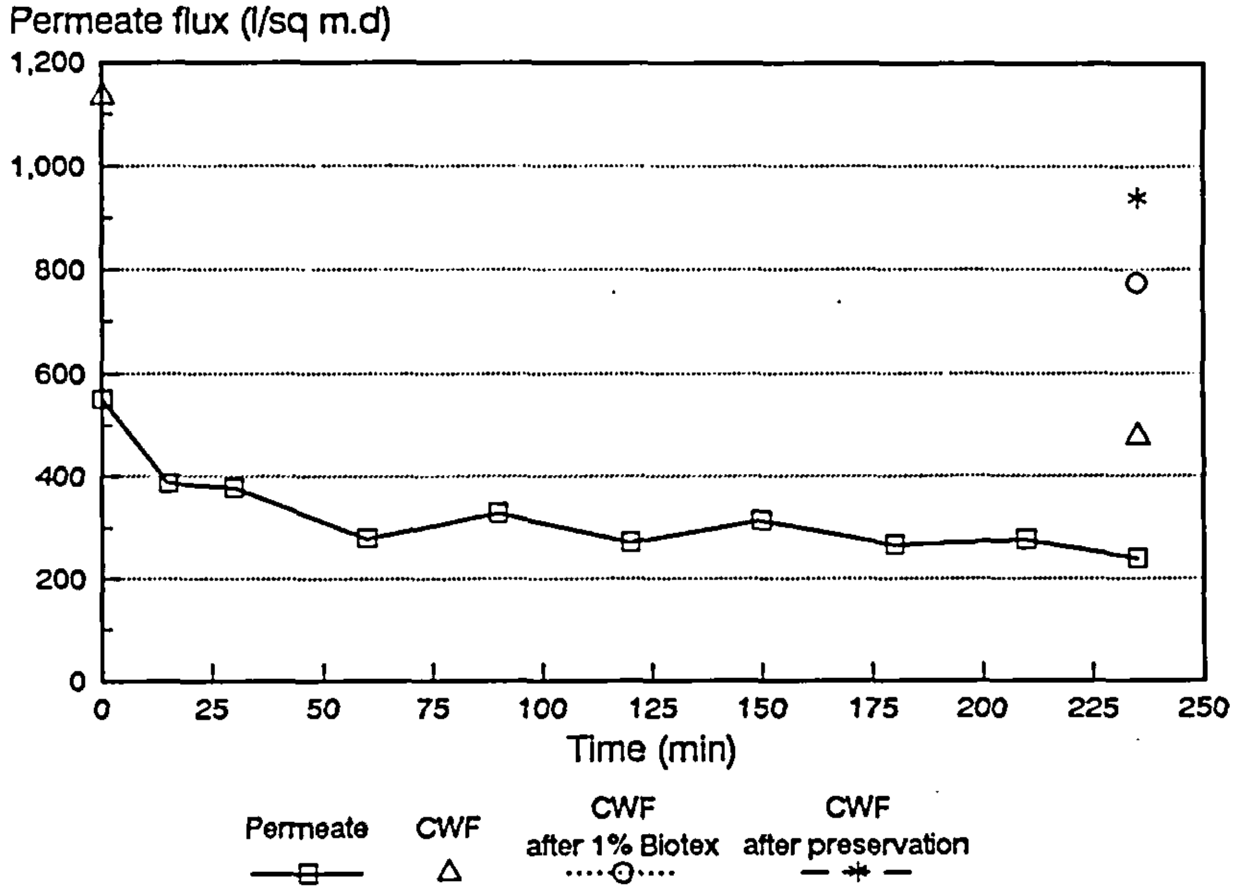

Figure 40 : Permeate flux as a function of time during UF treatment of the deliming effluent (polysulphone UF membranes).

Permeate flux as a function of percentage water recovery for the liming and deliming effluents is shown in Figure 41. Water recovery was approximately 90 percent.

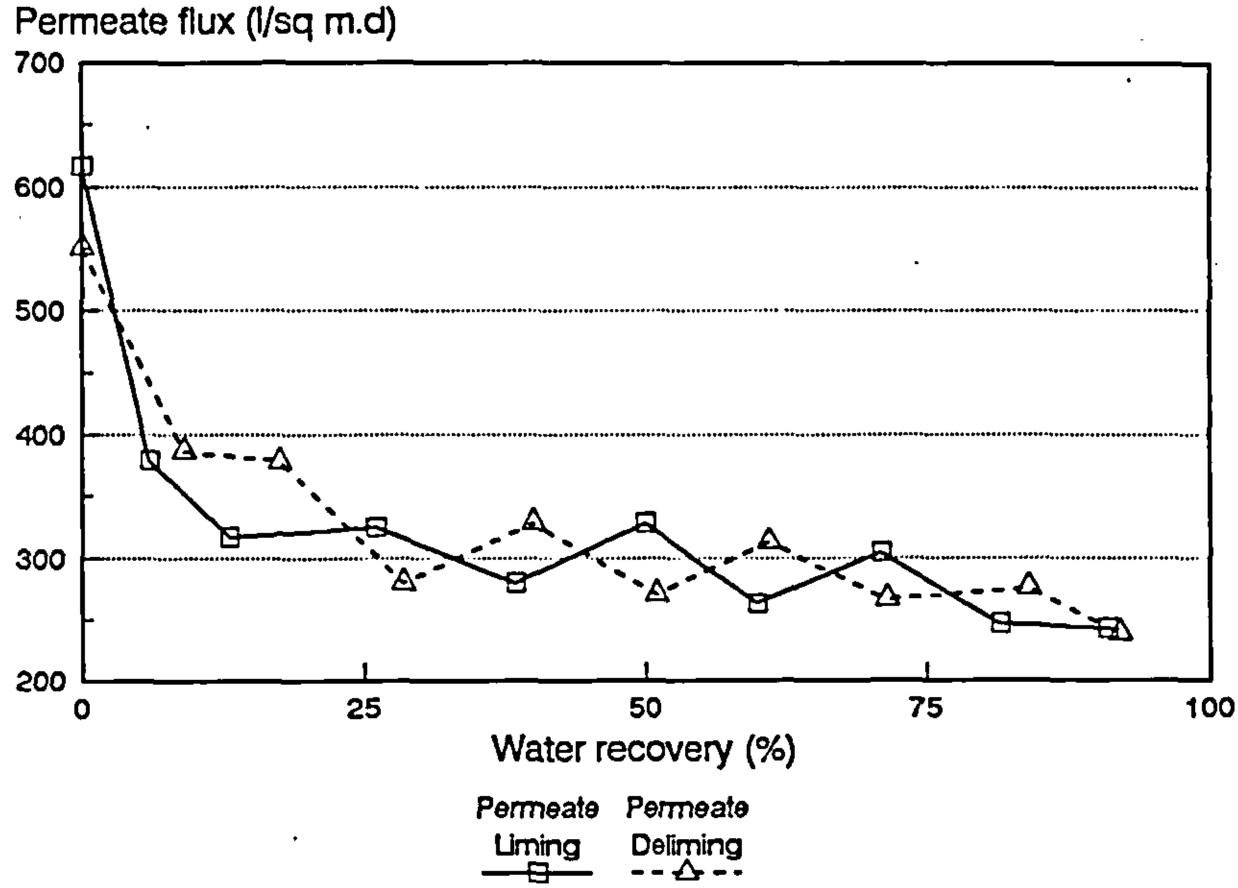

Figure 41 : Permeate flux as a function of water recovery during UF treatment of the liming and deliming effluents (polysulphone UF membranes).

9.2 Chemical composition of the UF feed, permeate and brine

The chemical composition of the UF feed, permeate and brine of the liming and deliming effluents is shown in Table 30. The pH, electrical conductivity, COD, alkalinity, chloride, suspended solids, calcium and sodium concentration levels of both effluents are high. The chromium (vi) concentration level of the deliming effluent also appears to be high (2,0 mg/ℓ).

Excellent COD removals were obtained. COD was removed from 21 650 mg/ℓ to 3 750 mg/ℓ in the UF permeate in the case of the liming effluent (82,7% removal). In the case of the deliming effluent, COD was removed from 16 500 to 3 580 mg/ℓ (78,3% removal). Excellent suspended solids removals were also obtained.

Table 30 : Chemical composition of UF feed, product and brine (liming and deliming effluents)

Constituents	Liming Effluent			Deliming Effluent		
	Feed	Permeate	Brine	Feed	Permeate	Brine
pH	12			12,29		
Conductivity (mS/m)	1 335	1 250	1 167	1 700	1 754	1 497
COD	21 650	3 750	67 600	16 500	3 580	53 000
Ammonia-N	25,67			21,05		
Nitrate-N	1,82			1,04		
Chloride	2 249			2 520		
Alkalinity	4 697			5 061		
Sulphate	900			900		
Suspended solids	3 240			—		
TDS	18 400			17 350		
Chromium	2,9			2,2		
Chromium (vi)	0,2			2,0		
Iron	13,5			15,1		
Potassium	104			70		
Sodium	1 893			2 100		
Magnesium	22,5			15,2		
Calcium	1 330			1 390		

9.3 Reverse osmosis treatment of the liming and deliming effluents

Permeate flux as a function of time and percentage water recovery for the liming effluent is shown in Figures 42 and 43. Permeate flux started at 769 $\ell/m^2.d$ and was 540 $\ell/m^2.d$ at the end of the run. The average permeate flux was calculated at 687,5 $\ell/m^2.d$. No decline in CWF was observed. Water recovery was 82 percent (Figure 43).

Permeate flux as a function of time and percentage water recovery for the deliming effluent is shown in Figures 44 and 45. Permeate flux was 715,5 $\ell/m^2.d$ when the run was started and was measured at 344,6 $\ell/m^2.d$ at the end of the run. The average permeate flux was 467 $\ell/m^2.d$. No decline in CWF was observed. Water recovery was approximately 80 percent (Figure 45).

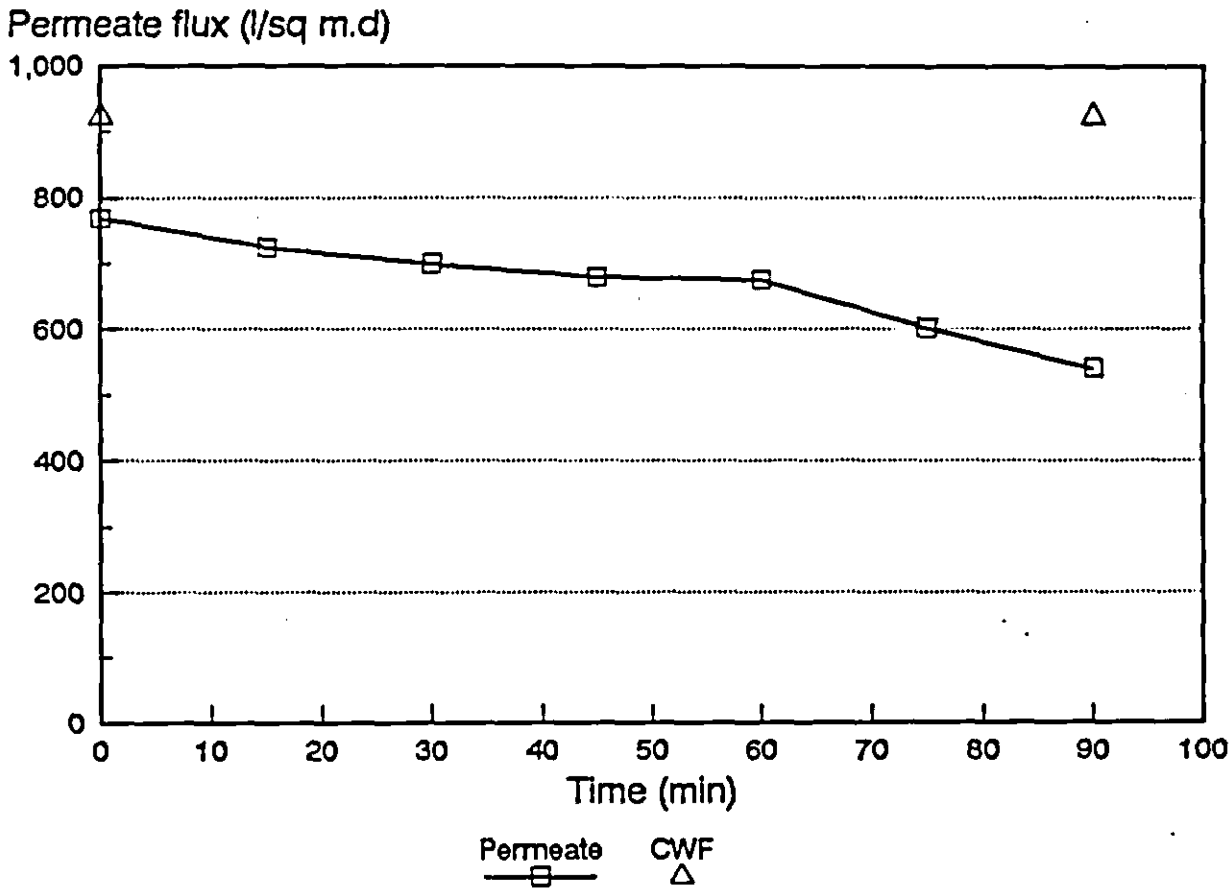

Figure 42 : Permeate flux as a function of time during RO treatment of the liming effluent (cellulose acetate RO membranes).

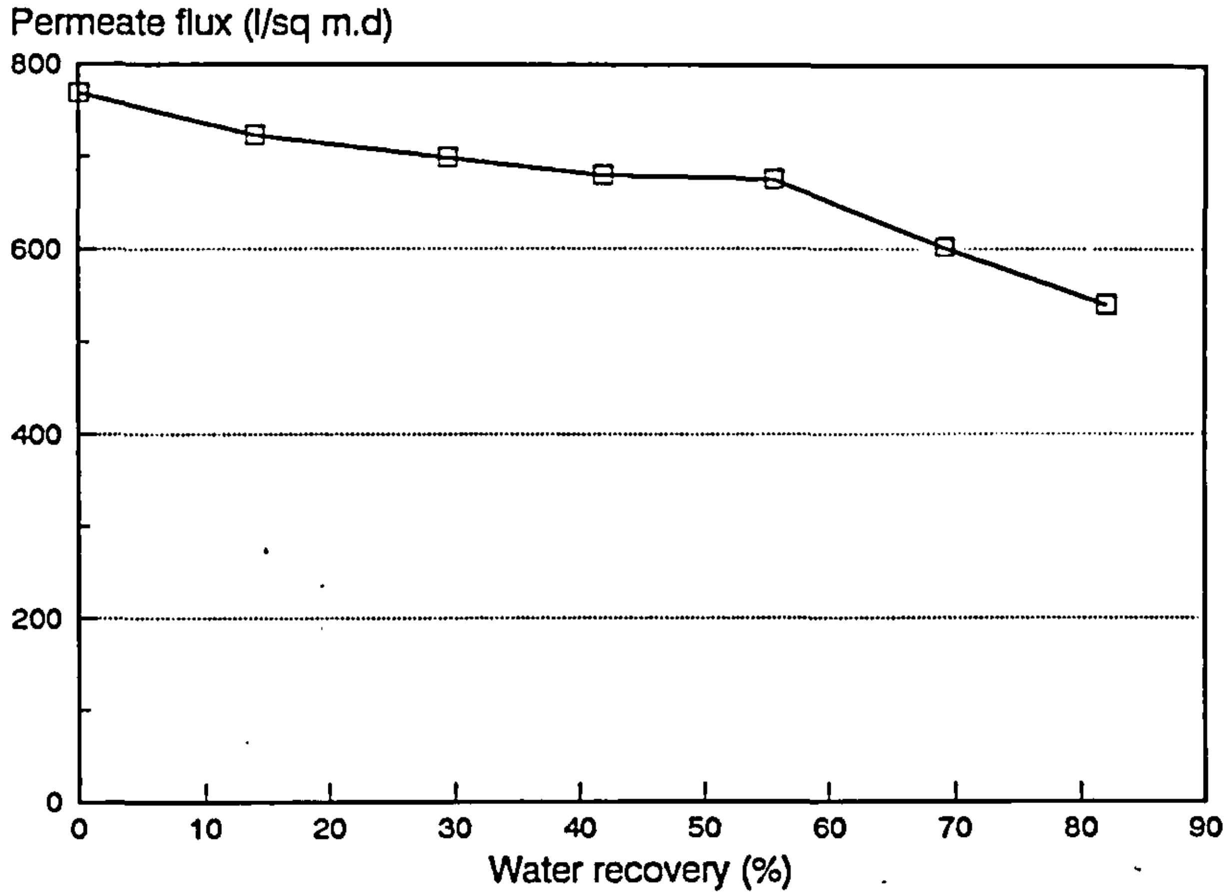

Figure 43 : Permeate flux as a function of percentage water recovery during RO treatment of the liming effluent (cellulose acetate RO membranes).

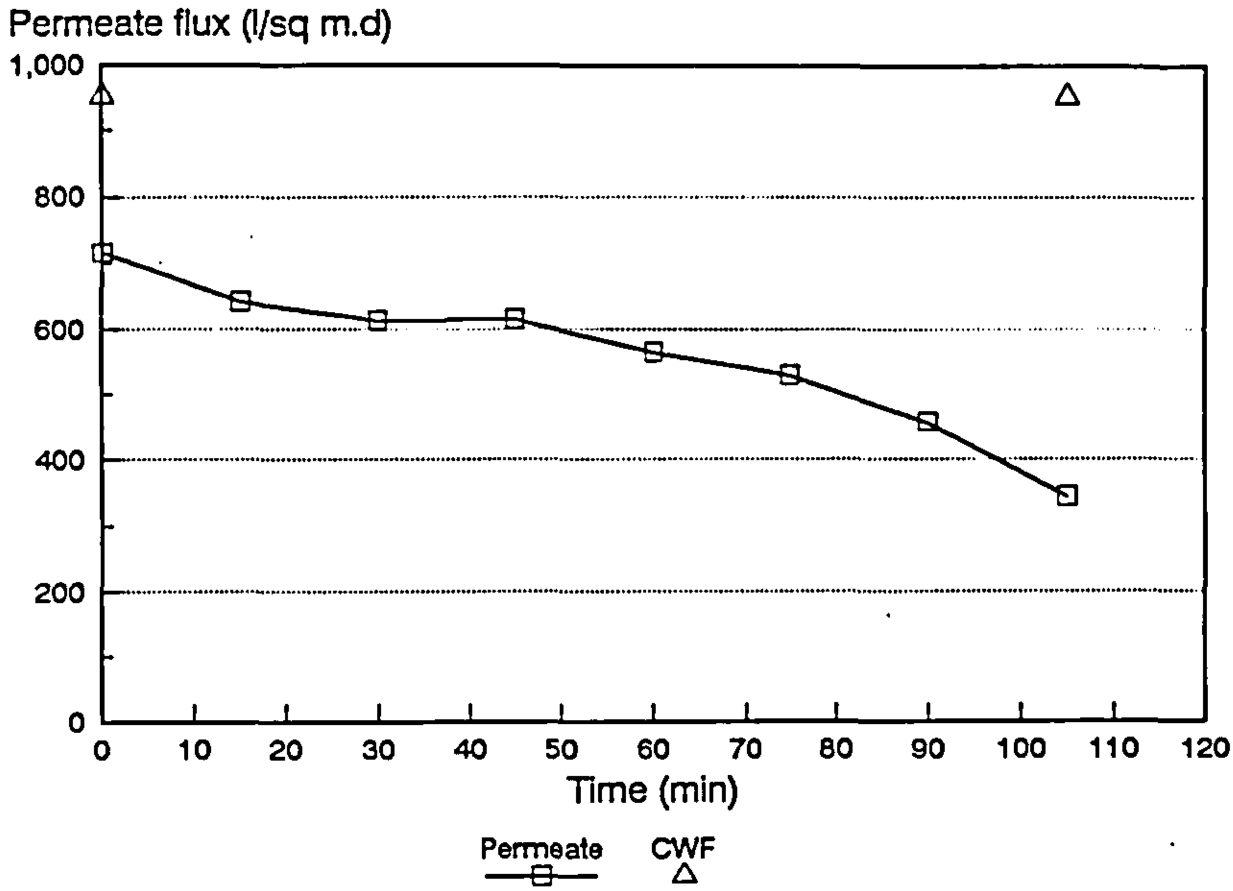

Figure 44 : Permeate flux as a function of time during RO treatment of the deliming effluent (cellulose acetate RO membranes)

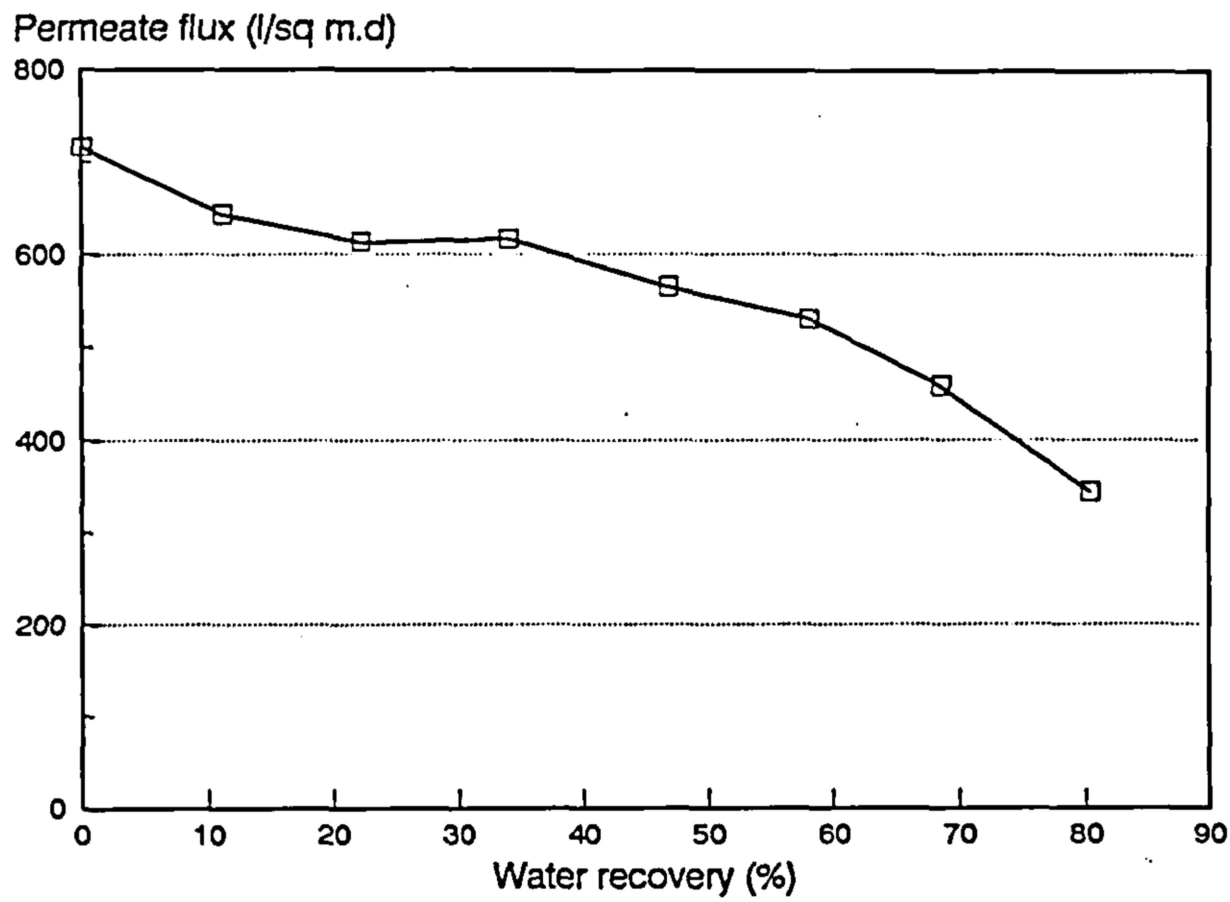

Figure 45 : Permeate flux as a function of percentage water recovery during RO treatment of the deliming effluent (cellulose acetate RO membranes).

9.4 Chemical composition of RO feed, permeate and brine

The chemical composition of the RO feed, permeate and brine of the liming and deliming effluents is shown in Tables 31 and 32, respectively.

Hydrogen sulphide was evolved during pH adjustment of the UF permeate to a pH of less than 7 with hydrochloric acid (30 - 33% HCl) prior to RO treatment. A white precipitate formed in the acidified feed. No attempt was made to analyze the precipitate. The RO permeate became milky after standing for approximately 10 minutes.

A relatively good quality RO permeate could be produced. The electrical conductivity of the RO feed was reduced from 654 to 154 mS/m (76,5% removal). However, it was expected that a higher percentage removal of salinity would be possible. The lower salinity removal could be ascribed to a partially fouled membrane surface. However, relatively good ion rejections were obtained and it might be possible to reuse the RO permeate in a tannery. This matter should be investigated.

Table 31 : Chemical composition of RO feed, permeate and brine (liming effluent)

Constituents	Liming effluent			Rejection (%)
	Feed	Permeate	Brine	
pH	6,39	6,71	7,43	
Conductivity (mS/m)	654	154	1 963	76,45
COD	3 100	280	8 800	90,97
Ammonia-N	27,78*	14,35*	23,51*	48,34
Nitrate-N	0	0	0	—
Chloride	2 586	343,4	5 810	86,72
Alkalinity	324	22	812	93,21
Sulphate	290	27	1 250	90,69
TDS	7 448	1 020	24 772	86,31
Chromium	0,5	0,2	0,6	60,00
Iron	0,11	0,02	0,2	81,82
Potassium	80	16,7	263	79,13
Sodium	1 368	214	3 860	84,36
Magnesium	4,41	0,29	23,1	93,42
Calcium	650	60	2 200	90,77

*Interference with analysis experienced.

Brine volume comprised approximately 20 percent of the treated feed. The salinity of the brine is high. Major ions in the brine include sodium, chloride, sulphate and calcium. The COD of the brine is also high. Brine should be disposed of safely.

Hydrogen sulphide was also evolved when the ultrafiltered deliming effluent was neutralised with hydrochloric acid prior to RO desalination. The RO permeate also became milky on standing.

The electrical conductivity of the RO feed was reduced from 1 017 mS/m to 349 mS/m (65,7% removal). This relatively low conductivity removal can also be ascribed to a partially fouled membrane surface. However, a relatively good quality RO permeate was produced. The major ions present in the RO permeate are sodium and chloride.

The RO brine comprises approximately 20 percent of the RO feed. The major ions present in the RO brine are sodium, chloride, calcium and sulphate. The COD of the brine is also high. The brine should be disposed of safely.

Table 32 : Chemical composition of RO feed, permeate and brine (deliming effluent)

Constituents	Deliming effluent			Rejection (%)
	Feed	Permeate	Brine	
pH	6,81	6,99	7,90	
Conductivity (mS/m)	1 017	349	1 552	65,68
COD	3 350	620	9 200	81,49
Ammonia-N	25,68*	31,97*	23,94*	—
Nitrate-N	0	0	0	—
Chloride	3 266	650,6	9 153	80,08
Alkalinity	704	247	2 141	64,91
Sulphate	500	65	3 600	87,00
TDS	10 436	1 940	37 704	81,41
Chromium	0,4	0,3	1	25,00
Iron	0,18	0,01	0,6	94,44
Potassium	59	22	246	62,71
Sodium	1 860	464	6 730	75,05
Magnesium	0,39	0,19	11,6	51,28
Calcium	817	51,2	4 100	93,73

*Interference with determination of concentration levels.

10. GENERAL DISCUSSION

Tannery effluents from Hanni Leathers at Nigel were used for the study. The study was conducted on site and in the process laboratories of Watertek in Pretoria. Effluents from Hanni Leathers Tannery can be considered as an example of model effluents of tanneries in South Africa. This is the reason why Hanni Leathers has been selected for the study.

The major problem with the discharge of tannery effluents into the municipal sewerage system is that it increases the salinity level of the municipal sewerage system which eventually causes an increase in the salinity levels of surface waters. High concentration levels of ammonia-nitrogen, sulphides, chromium and COD are also discharged into the municipal treatment system. All this is unacceptable to the municipal authorities. Therefore, ways and means should be sought to treat tannery effluent successfully so that it would not have adverse effects on the water environment.

Most of the salinity discharged by tannery effluents is concentrated in a relatively small percentage of the total effluent volume discharged by a tannery. The salinity level in some of the smaller streams may be too high for effective treatment with membrane desalination processes. However, different routes are available which can be used for treatment of tannery effluents with membrane technology.

Different options are available for treatment of tannery effluents. The final combined effluent can be treated or effluent streams within the process can be segregated and treated. Both these options were evaluated in this study. It was demonstrated that it should be possible to treat the final combined effluent successfully with a combination of UF and RO for salinity and organics removal. It was also demonstrated that it should be possible to treat segregated streams (soak paddle effluent, liming and deliming effluents, dye-house effluents) successfully with a combination of UF and RO for salinity and organics removal. However, the best way to treat these effluents should be dictated by the economics of the treatment processes under consideration. The economics of the treatment processes for the different streams have not been determined and it is suggested that the economics of the treatment processes for the different streams should be determined to give an indication of the most suitable stream to be treated for salinity and organics removal.

Low ion rejections were obtained during RO desalination in certain cases. These low ion rejections can be ascribed to membrane fouling. No membrane foulants were identified analytically. However, it is necessary that the membrane foulants be identified so that membrane fouling can be properly countered by the correct selection of membrane cleaning agents.

Polymeric ultrafiltration membranes were used in this study. Ceramic ultrafiltration membranes are more resistant to membrane fouling by organics in the sense that these membranes can be cleaned under more extreme conditions than polymeric membranes. The membrane life time of ceramic membranes can also be significantly longer than that of their polymeric counterparts. Therefore, it will be worthwhile to evaluate ceramic ultrafiltration and/or microfiltration membranes for treatment of tannery effluents prior to RO desalination.

11. CONCLUSIONS

- The final effluent produced by Hanni Leathers, despite pretreatment in a Silflo unit, fouls polysulphone UF membranes seriously. Ultrafiltration permeate flux was low. Permeate flux varied between approximately 100 and 400 $\ell/m^2.d$. However, it appears that it should be possible to control membrane fouling by pH adjustment of the effluent and regular cleaning of the membranes with a warm water rinse followed by cleaning of the membranes with an enzymatic cleaning and oxidizing agent.

- The COD of the UF feed varied between 1 500 and 4 000 mg/ℓ over the test period. However, poor COD removals were obtained. COD removals varied between 6 and 32 percent. This showed that most of the organics in the effluent had a relatively low molecular mass (40 000 mol mass cut-off UF membranes were used).

- Chromium, iron, sulphide and fats and oil removals were obtained with UF treatment of the effluent. These chemicals are all potential membrane fouling agents which could have contributed to varying degrees to the UF membrane fouling that has been experienced. However, no membrane foulants were removed from the surface of the membranes and analytically identified. Further work should be directed to identifying the membrane foulants analytically.

- Membrane fouling was experienced when the final effluent was treated with UFRO (polysulphone UF and PCI AFC 99 nanofiltration RO membranes). Low permeate fluxes were experienced. Ultrafiltration and RO permeate fluxes of approximately 150 to 500 ℓ/m^2.d and 100 to 150 ℓ/m^2.d were experienced, respectively. Fouling of the RO membranes was experienced despite the use of ultrafiltered water as feed to the RO membranes. It was noticed that the UF permeate became milky on standing. This could be ascribed to coagulation / flocculation of proteins in the effluent. It was most probably this material that was responsible for the membrane fouling that was encountered and this material should be analytically identified.

- Low electrical conductivity removals were obtained with the nanofiltration RO membranes. The feed electrical conductivity to the RO membranes varied between approximately 600 and 2 500 mS/m. The electrical conductivity of the RO permeate varied between approximately 500 and 1 500 mS/m. Therefore, poor electrical conductivity removals were obtained. Electrical conductivity removals varied between approximately 29 and 37 percent. The low electrical conductivity removals can be ascribed to the high percentage of monovalent ions in the RO feed compared to the divalent ions.

- Good COD removals were obtained with the nanofiltration RO membranes. The COD of the RO feed varied between 1 250 and 2 300 mg/ℓ. Permeate COD varied between 600 and 900 mg/ℓ. Therefore, COD removal varied between 20 and 66 percent.

- Membrane fouling was experienced during UFRO treatment of the final effluent when polysulphone UF (80% recovery) and cellulose acetate RO (70% recovery) membranes were used. The UF permeate flux was low (approximately 250 ℓ/m^2.d). It also appeared that it should be possible to control UF membrane fouling with regular chemical cleaning.

Relatively low permeate fluxes were experienced during RO treatment of the UF permeate. Permeate flux varied between 110 and 350 ℓ/m².d. Membrane fouling was also experienced despite the UF permeate that was used as feed to the RO unit. However, it appeared that it should be possible to control membrane fouling with regular chemical cleaning. Reverse osmosis brine comprises approximately 30 percent of the RO feed. The brine contains high concentration levels of inorganics and should be disposed of safely.

- Good electrical conductivity removals were obtained with the cellulose acetate RO membranes. The feedwater conductivity (UF permeate) varied between 2 580 and 4 290 mS/m over the test period. Permeate electrical conductivity varied between 300 and 753 mS/m. Electrical conductivity removal varied between 83 and 88 percent. Therefore, a relatively good quality water could be produced with RO. The electrical conductivity of the RO permeate also remained reasonably constant over the test period showing that severe membrane fouling was not experienced. Brine electrical conductivity levels were 2 980 and 4 020 mS/m in two cases. Brine also contains high concentration levels of ammonia-nitrogen (1 010 and 1 130 mg/ℓ); chromium (1,2 and 3,4 mg/ℓ); and fluoride (4,1 and 7,7 mg/ℓ). Therefore, brine should be disposed of safely.

- The COD of the RO feed (UF permeate) varied between 2 500 and 5 160 mg/ℓ. The COD of the RO permeate varied between 500 and 1 090 mg/ℓ during the test run. COD removals varied between 72 and 90 percent. Therefore, good COD removals were obtained with RO. However, a significant amount of low molecular mass organics were not removed by the RO membranes.

- Good turbidity and COD removals were obtained with alum coagulation / flocculation of the soak paddle effluent. Turbidity could be removed from 1 750 to 60 NTU (96,0% removal) at an Al^{3+} dosage of 150 mg/ℓ. COD was removed from 12 000 to 3 400 mg/ℓ (71,7% removal).

- Excellent turbidity removal was obtained from the soak paddle effluent with CFMF (polyester membranes). Turbidity was in one case removed from 1 700 NTU in the feed to 3,5 NTU in the permeate. COD was removed from 12 000 mg/ℓ in the feed to 6 730 mg/ℓ in the permeate (43,9% removal).

- Poor results were obtained with RO treatment of a concentrated soak paddle effluent. Electrical conductivity was removed from 7 160 to 3 830 mS/m (46,5% removal) at a water recovery of approximately 70 percent. COD was removed from 2 790 to 890 mg/ℓ (68,1% removal). The average permeate flux during a batch RO run was 75,5 ℓ/m².d. The low flux could be ascribed to membrane fouling and a high osmotic pressure of the feed. The electrical conductivity and COD of the brine were high, 10 780 mS/m and 5 830 mg/ℓ, respectively. Therefore, the brine should be disposed of safely.

- Better results were obtained with RO treatment of a more dilute soak paddle effluent. Feed electrical conductivity was reduced from 2 700 to 509 mS/m in one case (81,1% removal, water recovery approximately 80%). The average permeate flux was 200 ℓ/m^2.d. Ammonia-nitrogen was removed from 77,98 to 21,8 mg/ℓ (72,8% removal). COD was removed from 1 070 to 125 mg/ℓ (88,3% removal). Brine volume comprised 20 percent of the treated volume. Brine electrical conductivity was 7 010 mS/m in this case and the ammonia-nitrogen concentration was 165 mg/ℓ . The fluoride, sodium and chloride concentration levels were 9,9; 13 630; and 21 225 mg/ℓ, respectively. Therefore, the brine should be disposed of safely.

- Good results were obtained with treatment of the sump effluent (effluent from soak paddles, fleshing, splitting, deliming) with RO. Electrical conductivity was removed from 1 104 to 128 mS/m (88,4% removal). COD was reduced from 3 720 to 90 mg/ℓ (97,5% removal). The average permeate flux was determined at 330,5 ℓ/m^2.d. It appears that it should be possible to control membrane fouling with regular chemical cleaning. The electrical conductivity (3 620 mS/m) and COD (4 330 mg/ℓ) of the brine were high. The brine comprises 12,5 percent of the treated water and should be disposed of safely.

- Membrane fouling was experienced during treatment of the dye-house effluent with UF. Preliminary work, however, has indicated that it should be possible to control membrane fouling with regular chemical cleaning. Permeate flux was low (approximately 144 ℓ/m^2.d). Water recovery was 90 percent. A COD removal of 67,5 percent was obtained (removed from 22 900 to 7 440 mg/ℓ). The brine (10% of feedvolume) contained 79 000 mg/ℓ COD and the electrical conductivity was 1 307 mS/m. This brine should be disposed of safely.

- Membrane fouling was also experienced during RO treatment of the UF permeate. Preliminary work, however, has indicated that it should be possible to control membrane fouling with chemical cleaning. The average permeate flux was determined as 272 ℓ/m^2.d during a batch run. Water recovery was 80 percent. The feed electrical conductivity was reduced from 1 181 mS/m to 156 mS/m (86,8% removal). Ammonia-nitrogen and COD were removed from 456,1 to 64,2 mg/ℓ (85,9% removal) and 6 710 to 963 mg/ℓ (85,7% removal), respectively. The electrical conductivity (3 480 mS/m) and ammonia-nitrogen (1 494 mg/ℓ) concentration levels in the brine were high. The chromium (vi) concentration level in the brine was also high (2,0 mg/ℓ). Therefore, the brine should be disposed of safely.

- Membrane fouling was experienced during treatment of the liming effluent with UF. Permeate flux was low (approximately 290 ℓ/m^2.d). However, preliminary work showed that it should be possible to restore permeate flux with chemical cleaning. Water recovery was approximately 90 percent. A COD removal of 82,7 percent was obtained (removed from 21 650 mg/ℓ in UF feed to 3 750 mg/ℓ in UF permeate). The electrical conductivity of the UF brine (1 167 mS/m) as well as the COD were high (67 600 mg/ℓ). The chromium (vi) concentration level of the brine was also high (0,2 mg/ℓ). Therefore, the brine should be disposed of safely.

- Preliminary work showed that little, if any, membrane fouling occurred during treatment of the ultrafiltered liming effluent with RO. The average permeate flux was determined at 687,5 ℓ/m^2.d. Water recovery was 82 percent. The electrical conductivity of the RO feed was reduced from 654 to 154 mS/m (76,5% removal). COD was removed from 3 100 mg/ℓ in the RO feed to 280 mg/ℓ in the RO permeate (90,97% removal). The electrical conductivity (1 963 mS/m) and the COD (8 800 mg/ℓ) of the brine were high. Therefore, the brine should be disposed of safely.

- Membrane fouling was experienced when the deliming effluent was treated with UF. Permeate flux was low (approximately 264 ℓ/m^2.d). It was not possible to restore the CWF completely after chemical cleaning as was the case with the liming effluent. Further work will be required to evaluate membrane cleaning agents for membrane cleaning. Water recovery was approximately 90 percent. The COD of the effluent was reduced from 16 500 to 3 580 mg/ℓ (78,3% removal). The electrical conductivity (1 700 mS/m) and the chromium (vi) (2,0 mg/ℓ) concentration level of the deliming effluent were high.

- Preliminary work has shown that almost no membrane fouling took place during treatment of the deliming effluent with RO. The permeate flux (average flux) was determined at 467 ℓ/m^2.d. Water recovery was approximately 80 percent. The electrical conductivity of the RO feed was reduced from 1 017 mS/m to 349 mS/m (65,7% removal) and the COD from 3 350 to 620 mg/ℓ (81,5% removal). The electrical conductivity (1 552 mS/m) and COD (9 200 mg/ℓ) of the RO brine were high and should be disposed of safely.

12. ACKNOWLEDGEMENT

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