EVALUATION OF MICROFILTRATION, ULTRAFILTRATION AND NANOFILTRATION FOR SALT AND CHROMIUM RECOVERY FROM SPENT PICKLING AND TANNING EFFLUENT

JJ Schoeman

WRC Report No. 1370/1/04

Water Research Commission

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Report to the Water Research Commission

by

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WRC Report No. 1370/1/04
ISBN No. 1-77005-107-5

FEBRUARY 2004

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Printed by Silowa Printers: 012 804 7565

EXECUTIVE SUMMARY

BACKGROUND

Leather manufacturing effluents contain high concentrations of sodium chloride and chromates which are used in the pickling and tanning processes, respectively. Consequently, the South African leather industry is under pressure from the authorities to reduce the pollution load in effluent discharged into the water environment. Brine effluents from the pickling/tanning processes are normally not reused because of poor quality and fear of affecting leather quality adversely.

Chromium and salt in the pickle/tanning stage effluent have the potential to be recovered for reuse in the pickling/tanning process. Such an action will prevent water pollution from taking place and the increasing mineralisation of our scarce water resources. Resources will also be conserved in the process especially when water can be recovered for reuse by desalination of the final effluent produced by tanneries.

Environmentek and the previous LIRI Technologies have demonstrated in laboratory scale studies that microfiltration and/or ultrafiltration and nanofiltration, should function effectively for chromium and salt recovery from neutralized spent pickling/tanning effluent. However, the degree of purity of the recovered chrome and salt for reuse in the tanning/pickling process as well as the continuous use of the chemicals on leather quality are unknown factors. Little information is available regarding process efficiency for chroming and salt recovery and the removal of organics from the spent tanning/pickling effluent. Insufficient information is also available regarding the fouling potential of the effluent for the membranes and procedures to clean the fouled membranes. No information is also available regarding the acceptability of such an approach by the tannery industry, the economics of such an approach and the international use of membrane technology for this application. Therefore, the required information should be obtained prior to any further studies.

Environmentek has also demonstrated in previous studies that a combination of ultrafiltration and reverse osmosis should function effectively for the desalination of the final effluent, produced by tanneries. Severe membrane fouling, however, was experienced and procedures to clean the fouled membranes were not completely solved. Little information is also available on the economics of the process, the acceptability of the approach by the South African leather industry and the international use of membrane technology for this application. Therefore, the required information should be obtained before any further action in this regard.

AIMS

The main of this investigation was to conduct a techno-economic study to establish the viability of developing microfiltration/ultrafiltration/nanofiltration process technology for the recovery of chromium and salt from spent pickling/tanning effluent for reuse in the process. The secondary aims of the investigation was to establish the viability of developing ultrafiltration/reverse osmosis technology for the desalination of the final effluent produced by tanneries.

The techno-economic study was conducted to : -

(i) establish the international use of membranes for the applications and;
(ii) obtain an indication of the economic feasibility and acceptability of the use of membrane technology in the South African leather industry.

METHODOLOGY

The techno-economic feasibility of the processes were determined from literature information, and from discussions with experts in the leather industry. The acceptability of the use of membrane technology in the leather industry was also determined from discussions with experts in the South African and overseas leather industries.

CONCLUSIONS

Chromium tannage

It was shown in experimental studies that a combination of ultrafiltration and nanofiltration should be effectively applied for chromium recovery for reuse in the tanning process. The recovered chromium was used for tanning and treated skins were compared with control skins treated with fresh chromium solutions. Analysis conducted on the experimental skins shows values very similar to those obtained on the control group. Salt that permeated the nanofiltration membranes should be suitable for use in the pickling process.

Pickling

Reverse osmosis is proposed to treat the exhausted bath to recover salt for reuse in the pickling process. The reverse osmosis permeate should be suitable for the preparation of soaking baths and as washing water. However, experimental studies will be required to define the application.

Final effluent

It was experimentally demonstrated that it should be possible to apply reverse osmosis for the desalination of the final effluent produced by tanneries. The effluent, however, should be properly pretreated (physical/chemical methods) prior to reverse osmosis desalination. The treated effluent should comply to the discharge quality requirements. Membrane fouling, however, will be a problem during reverse osmosis treatment of the final effluent and fouling control will be an important aspect for the successful application of this technology. Pilot studies will be required to work out procedures for the application of this technology in the tannery industry.

Pilot studies conducted at a tannery in South Africa have indicated that the capital cost to treat the final effluent produced by the tannery with a combination of ultrafiltration and reverse osmosis will amount to approximately R12,0 million. Operating costs will amount to approximately R5,65/m^3.

High concentrations of organics in the final effluent should be reduced by a membrane bioreactor. The activated sludge should be concentrated sufficiently with ultrafiltration membranes for the successful aerobic or anaerobic degradation of high molecular mass organics in the effluent. The ultrafiltration permeate containing less organics should be suitable for further desalination of the effluent. However, pilot studies will also be required to establish procedures for the successful implementation of the technology at tanneries.

Other effluents in a tannery

Ultrafiltration is proposed for the treatment of the soaking, deliming-bating, degreasing and vegetable tannage effluents. However, pilot studies will be required to define the applications.

The reverse osmosis process is proposed for the recovery of dyeing substances for reuse in the dyeing process. The permeate should be suitable as washing water for the preparation of new dyeing baths. However, pilot studies will be required prior to implementation of this technology at tanneries.

Ultrafiltration is at present applied on a commercial scale for the recovery and reuse of sulphide from the unhairing process. This appears to be the only full-scale application of membrane technology in the tannery industry at present.

Direct and Indirect energy savings

Membrane processes integrated with chrome and salt recovery (UF and NF), unhairing-liming (UF) and degreasing (UF) treatment have been determined to be energetically economical. Therefore, it should be viable to develop microfiltration/ultrafiltration/-nanofiltration process technology for the recovery of chromium and salt from spent pickling/tanning effluent in South Africa for reuse in the process.

Opinion of overseas and South African leather experts

Overseas leather experts are of the opinion that there are only a handful of membrane plants at present in operation overseas within the tanning sector, primarily in Italy and primarily for the treatment of process liquor for chemical recovery. Reverse osmosis and nanofiltration appear not to be applied at present although different groups are working on these technologies for potential application for effluent desalination and chemical recovery.

South African leather experts are of the opinion that salt pollution caused by the tannery industry should be addressed by the proper technology. Most of the South African leather experts, however, are not very familiar with membrane separation technology as a means for effluent treatment. However, membrane technology will be an acceptable technology for the treatment of tannery effluent once a track record has been established. At present membrane technology appears not to be economically feasible for the treatment of tannery effluent in South Africa due to the low charges for effluent disposal. However, there will be no choice as to treat tannery effluent with membrane technology when it becomes more expensive to discharge tannery effluent or when the effluent discharge standards become stricter. Tanneries also might loose business if they do not comply with the regulations of the Environmental standards. Consequently, it is foreseen that membrane technology will in future play a role in the treatment of tannery effluent for pollution control and for water and chemical recovery for reuse.

ACKNOWLEDGEMENTS

The project leader wishes to thank the following persons for their valuable input into the investigation :

Mr J Barnard	Environtan, RSA
Mr N Sneider	Seton (Pty) Ltd., RSA
Mr P Howard	Pelts Products, RSA
Mr A Pratt	Bader Bob, RSA
Mr W Bowden	BLC Leather Technology Centre Ltd., UK
Mr G Clonfero	Environmental Engineer, Italy
Prof. E Drioli	University of Calabria, Italy

The financing of the project by the Water Research Commission is gratefully acknowledged.

ABBREVIATIONS

mld	:	Million dollar
COD	:	Chemical oxygen demand
BOD	:	Biochemical oxygen demand
RO	:	Reverse osmosis
UF	:	Ultrafiltration
MF	:	Microfiltration
NF	:	Nanofiltration
ED	:	Electrodialysis
NMWCO	:	Nominal molecular weight cut-off
ACF	:	Activated carbon filter
ETP	:	Effluent treatment plant
TDS	:	Total dissolved solids
kDa	:	kilo Dalton
CLR	:	Closed-loop recycle
B	:	Batch
VRF	:	Volume reduction factor
TSS	:	Total suspended solids
EUR	:	Euro
GG	:	Gigajoules
kWh	:	Kilowatt hour
UNIDO	:	United Nations Industrial Development Organization
LDPE	:	Low density polyethylene
TS	:	Total solids
Mlir	:	Million lire
UFRO	:	Ultrafiltration reverse osmosis
lmd	:	litre per square metre per day
CIP	:	Clean in place
V_∞	:	Velocity of the fluid
Km	:	Mass transfer coefficient
CRU	:	Chrome recovery unit
HS	:	Hair save

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1. INTRODUCTION

1.1 BACKGROUND

The leather industry is under pressure from the authorities to reduce the salt and chrome load in the effluent discharged to inland public water bodies. Sodium chloride is commonly used as a pickling agent in the production of leather. Chromates are used in the tanning process. Brine effluents from these processes are commonly not reused, because of poor quality and the fear of affecting leather product quality adversely.

Pickling stage effluent contains chrome 111 salts and organic contaminants. Chromium and salt, however, have the potential to be recovered and recycled in the pickling/tanning process. This will prevent water pollution and the increasing mineralisation of our scarce water resources. Resources will also be conserved in the process. (Note: Desalination of the final effluent produced by tanneries should also prevent mineralisation of water resources with the advantage that water can be recovered for reuse).

Environmentek and the previous LIRI Technologies have demonstrated in laboratory scale-studies that microfiltration (MF) and/or ultrafiltration (UF) should function effectively for chromium and salt recovery from spent pickling/tanning effluent (Schoeman and Steyn, 1998). However, the degree of purity of the recovered chrome and salt for reuse in the tanning/pickling process and the impact of the continuous use of the recovered chrome and salt on leather quality, are unknown factors. Procedures for chrome recovery (magnesium oxide, soda ash or lime neutralization followed by acid extraction) and reuse of salt are also not clear. Little information is also available on the fouling potential of the effluents for the membranes and ways and means to clean the fouled membranes. There is also little information available regarding process efficiency for chromium and salt recovery and organics removal from the spent tanning/pickling effluent. Process design criteria for a full scale application and the economics of the process are also unknown factors. Therefore, the required information should be obtained through laboratory and pilot demonstration studies to convince the tannery industry that technology is available that will help them to protect the environment and their business interests.

Environmentek has demonstrated that a combination of ultrafiltration and reverse osmosis (RO) technologies should function effectively for the treatment of the final effluent produced by tanneries (Schoeman and Steyn, 1996). However, information regarding cleaning strategies for the fouled membranes are not clear. Process design criteria for this alternative route to solve the effluent problems experienced by the tannery industry are also lacking.

1.2 AIMS

The main aim of this project was to perform a techno-economic study to establish the viability of developing microfiltration/ultrafiltration/nanofiltration (NF) process technology for the recovery of chromium and salt from spent pickling/tanning effluent for reuse in the process. The secondary aim of this project was to establish the viability of developing ultrafiltration/reverse osmosis technology for the desalination of the final effluent produced by tanneries.

The techno-economic study was done to : -

(i) establish the international use of membranes in the application, and

(ii) obtain an indication of the economical feasibility and acceptability of the use of membrane technology in the South African leather industry.

1.3 METHODOLOGY

A techno-economy study was conducted prior to any further local research to try to establish the international use of membranes for chromium and salt recovery from spent pickling/tanning effluent, as well as the use of membrane technology for the desalination of final effluent produced by tanneries. The techno-economic feasibility of the processes were determined from literature information, and from discussion with experts in the leather industry. The acceptability of the use of membrane technology in the leather industry was determined from discussions with experts in the South African and overseas leather industries. The obtained information will be used to determine to what extent further research should be done to develop processes for the treatment of tannery effluent in South Africa.

2. TECHNO-ECONOMIC STUDY – TREATMENT OF AQUEOUS EFFLUENTS OF THE LEATHER INDUSTRY BY MEMBRANE PROCESSES

2.1 BACKGROUND

The potential of membrane processes for the treatment of aqueous solutions coming from the leather industry was recently described by Cassano *et al.* (2001) and others (Schoeman and Steyn (1996); Schoeman and Steyn (1998); Cassano *et al.* (1997); Cassano *et al.* (1996); Cassano *et al.* (1999)).

The Italian leather industry, represented by about 2 400 tanneries, is an important sector of the national and international chemical industry. In 1997 sales of Italian leather manufacturing were about US$ 6 000 mld. This value represents 65% of the European Union sales and 15% of the world-wide production.

Italian tanneries are located in three main poles (Cassano *et al.* 2001) : -

Veneto, Toscana and the Campania regions : These tanneries transform raw or wet-blue skins into products used for shoes manufacturing (50%), upholstery (18%), clothes and gloves (15%), leather goods (15%) and others (2%). This transformation requires a series of chemical and mechanical treatments. Chemical processes are conducted in chemical reactors (tumblers) in which the skins react with different chemicals (acids, alkalis, chromium salts, tannins, solvents, sulphides, dyes, auxiliaries, etc.) in aqueous solutions.

Wastewaters coming from the different operations contain high concentrations of organic and inorganic substances and can cause serious pollution problems. The leather industry has always been considered as one of the most polluting industries characterized by the low technological level of its operations.

Organic pollutants (proteic and lipidic components) come from skins (it is calculated that the raw skin has a 30% loss of organic material during the working cycle) or are introduced during the working cycle (for example tannins). Inorganic pollutants are residues of the used chemicals that are not completely fixed by the skins due to the low efficiency of the operations. Stricter regulations in terms of environmental protection will urge the leather industry to investigate new strategies for the recovery and recycle of chemicals and by-products coming from the working cycle.

The aqueous streams of each operation in the leather making process are generally mixed together and subsequently submitted to chemical, physical and biological treatments with the formation of sludges that are difficult to reuse and therefore forwarded into dumps.

In various industrialized countries the decision has been taken to reduce the tanning operations. The possibility to apply membrane processes in the treatment of the exhausted bath of a single step offers very interesting perspectives for the survival of this industry and for recovering and recycling of the primary resources (Molinari, 1995). Membrane processes can also be used for the treatment of the final effluent (global) produced by tanneries in order to remove the salt content or to separate the biomass from the effluent after chemical–physical treatments. The integration of advanced molecular separation technologies, as the membrane processes, in the productive lines, can make this industrial sector compatible with a sustainable growth according to Cassano *et al.*, (2001).

The main potential applications of membrane processes in various operations of the tanning cycle are described in this review (Cassano *et al.*, 2001). Some of them are already consolidated at industrial level. Others will be discussed on the basis of the results obtained on laboratory or pilot scale plants. For each application the scheme of the process operating conditions, pretreatment, fouling problems and relative cleaning operations will be discussed and compared to the results obtained by others.

A method for calculating the saving of direct and indirect energy is also applied in the various steps of the productive cycle.

2.2 EXPERIMENTAL RESULTS AND NEW PROPOSALS

Conventional technologies to reduce pollution problems of wastewaters are principally based on end-of-pipe treatments at present (Cassano *et al.*, 2001). In these processes the final effluent, produced by mixing the single exhausted baths, is submitted to chemical, physical and biological treatments. The use of these technologies is space-requiring and does not permit the recovery and recycling of chemicals and water. Consequently, the produced sludges are usually discharged into dumps although the sludges are containing primary resources which could be reused at industrial level.

The average composition and the volume percentage of the effluents for a specific tannery producing chromium tanned leather from which the global polluting load can be obtained is shown in Table 1 (Cassano *et al.*, 2001). To reduce these polluting parameters, new strategies propose the treatment of the single exhausted baths of the various wet phase operations. The advantage is to operate on solutions containing a high concentration of reusable substances and a lower quantity of undesirable components than present in the global effluent. In this way, the cleaning-up of residual effluent is simplified and it is possible to submit it to biological treatment: the produced sludges, rich in organic substances, could be reused in agriculture as fertilizer.

Research studies on the possibility to use membrane processes represent a very significant innovation in this sector. The experimental and proposed application in wet tanning operations are shown in Fig. 1 and are discussed in the following way (Cassano *et al.* 2001):

2.2.1 Soaking

In the soaking operation raw skins are treated with water and small quantities of imbibing substances in order to (Cassano *et al.*, 2001) : -

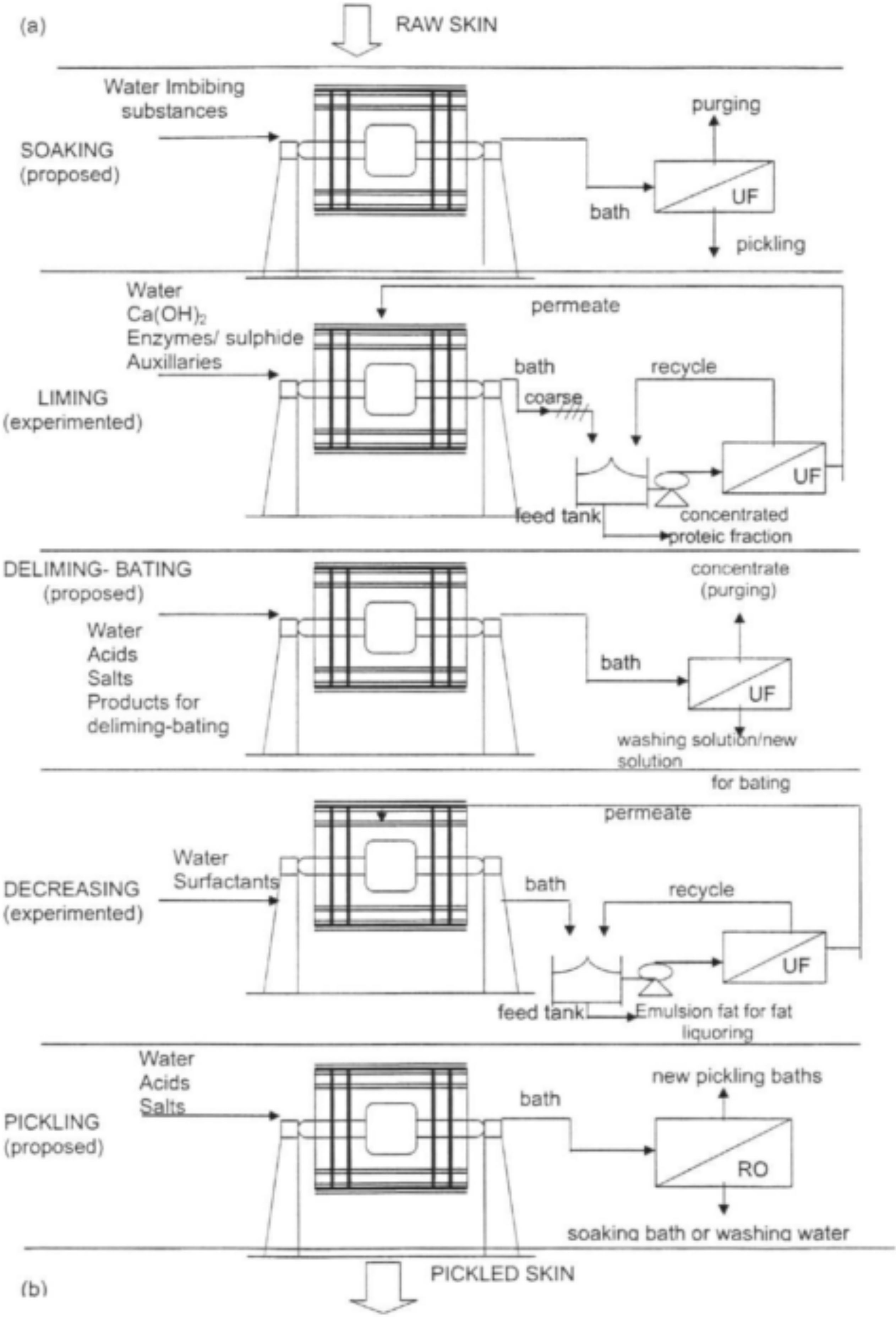
(a) hydrate the skin proteins;
(b) solubilize the denatured proteins;
(c) eliminate the salt used in the preservation step;
(d) hydrate and to open the contract fibres of the dried skins; and
(e) eliminate the dirt (blood, excrement, earth) stuck to the skin.

The exhausted bath of soaking therefore contains excrements, salts and chemical additives, and it is normally sent to a water treatment plant.

A new approach for the treatment of soaking effluent could be the use of ultrafiltration. However, pretreatments are necessary in order to remove suspended materials; sedimentation permits to reduce suspended solids by 90%; steel spring filters (200 – 300 μm net size) could be employed to remove large particles avoiding clogging of membranes. The organic components can next be concentrated in the feed tank of the UF plant and discharged. The clear permeate, rich in salt, could be reused in the pickling step after adjustment of the salt concentration by sodium chloride addition. This new approach, however, needs experimentation in order to obtain more data to define its application.

Table 1: Mean composition and volume percentage of various wet operations in a leather industry

Parameter	Soaking		Liming-bating		Deliming		Pickling	Chromium tanning	Dyeing, fat liquoring, retanning		Other effluents
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
pH	6	10	12,5	13	6	11	4	3,2	4	10	-
Temperature (°C)	10	30	10	25	20	35	-	-	20	60	-
Sedimentable materials (mg/ℓ)	100	250	300	700	50	150	20	45	100	500	-
Total suspended solids (mg/ℓ)	2 300	6 700	6 700	25 000	2 500	10 000	380	1 400	10 000	20 000	-
BOD_5	2 000	5 000	5 000	20 000	1 000	4 000	100	250	6 000	15 000	-
COD (mg/ℓ)	5 000	11 800	20 000	40 000	2 500	7 000	800	400	15 000	75 000	-
Chromium (III)(mg/ℓ)	-	-	-	-	-	-	-	4 100	0	3 000	-
Sulphides (mg/ℓ)	0	700	2 000	3 300	25	250	-	-	-	-	-
Chlorides (mg/ℓ)	17 000	50 000	3 300	25 000	2 500	15 000	8 950	2 000	5 000	10 000	-
Oils and fats (mg/ℓ)	1 700	8 400	1 700	8 300	0	5	-	-	20 000	50 000	-
Chlorinated solvents (mg/ℓ)	-	-	-	-	0	2 500	-	-	0	250	-
Surfactants (mg/ℓ)	0	400	0	300	0	500	-	-	500	2 000	-
Discharge water on total volume (%)	18		12		22		2	3	38		5



(a)
RAW SKIN
Water Imbibing substances
SOAKING (proposed)
purging
bath
UF
pickling
Water
$Ca(OH)_2$
Enzymes/ sulphide
Auxillaries
LIMING (experimented)
permeate
bath
coarse
recycle
UF
feed tank
concentrated proteic fraction
DELIMING- BATING (proposed)
Water
Acids
Salts
Products for deliming-bating
concentrate (purging)
bath
UF
washing solution/new solution
for bating
permeate
Water
Surfactants
DECREASING (experimented)
bath
recycle
UF
feed tank
Emulsion fat for fat liquoring
Water
Acids
Salts
PICKLING (proposed)
bath
new pickling baths
RO
soaking bath or washing water
PICKLED SKIN
(b)

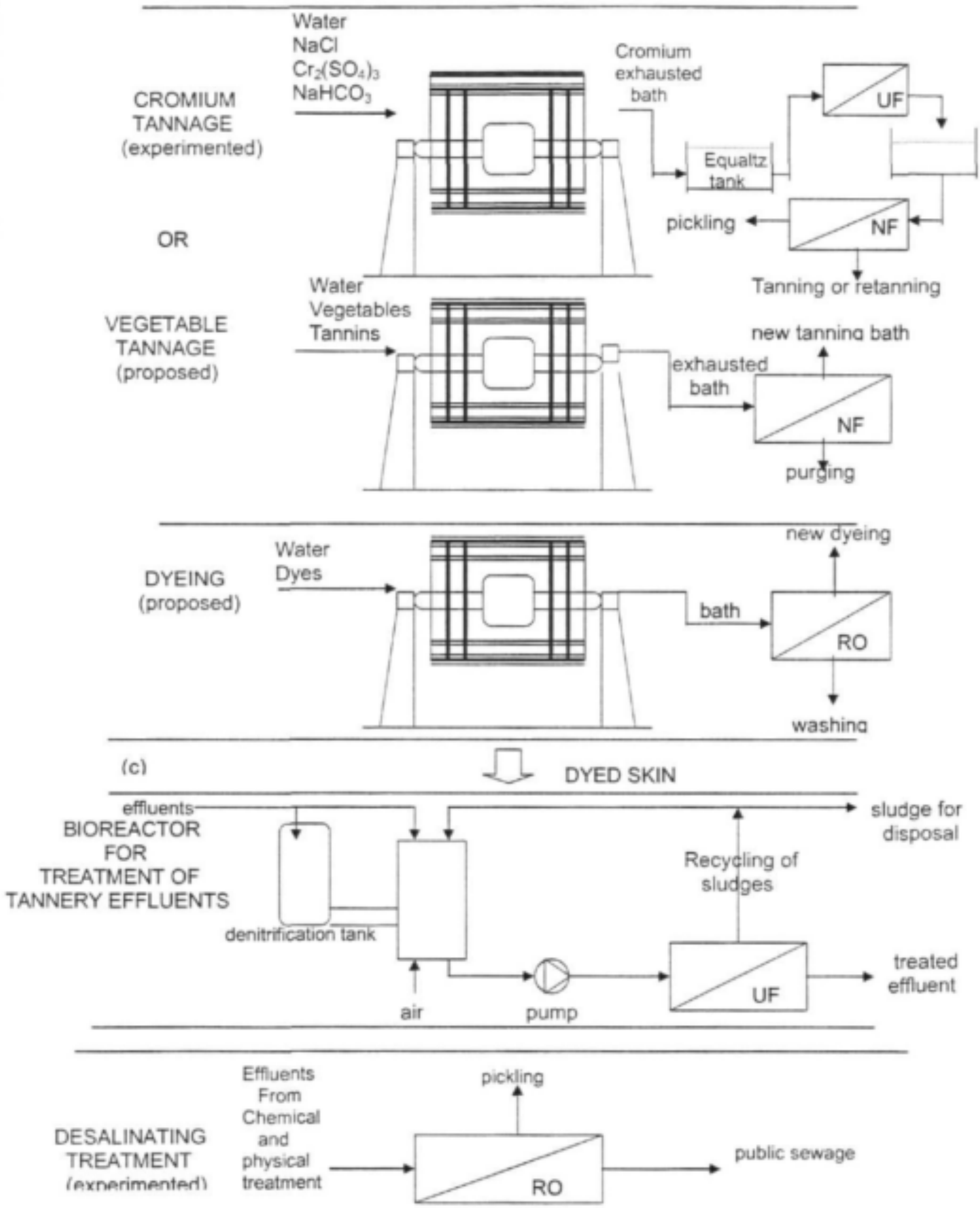


Figure 1. Schemes of various applications of membrane processes in the tanning cycle. Wet phases before tannage (a); tannage and dyeing (b); and treatment of final wastewaters (c)(Cassano *et al.*, 2001).

However, the recycling of fresh water and salt and the saving on wastewater cleaning-up cost should give lower costs as compared to similar applications in other fields.

2.2.2 Unhairing

The aim of the unhairing-liming treatment is the elimination of components from skins that are not transformed into leather, such as superficial epidermic matter including hair and the subcutaneous adipose layer (Cassano *et al.*, 2001). At the same time, as a consequence of an opening of the fibrous structure of derm, the reactivity of collagen towards tanning substances is improved.

The liming operation achieves: unhairing, partial saponification of the natural fats, elimination of most interfibrillar proteins (albumins, globulins, etc.), degradation and elimination of mucoids and swelling of the derm. Lime and sodium sulphide or sulphydrate are normally used to obtain these objectives (Martignone, 1997).

Liming-unhairing effluents are highly polluting as a result of the presence of sulphides, amines, by-products coming from degradation of hair and epidermis and high concentration of alkalis. The COD of this wastewater ranges between 20 000 and 40 000 mg/ℓ.

The application of UF to this type of stream (Molinari, 1995; Drioli and Molinari, 1986; Kleper, 1997; Aloy and Donikian, 1992), also at industrial level, permitted to recover, in the permeate, sulphide and solubilized lime containing low molecular weight proteic substances. This aqueous solution is reused for the preparation of a new liming bath. High molecular weight proteic components coming from the chemical degradation of hair and epidermis are concentrated in the retentate stream.

Tubular UF membranes made of carbon fibres permitted to obtain a rejection to protein of 60 – 85%. Using non-cellulosic UF tubular membranes (Abcor, HFM 180, cut-off 18 000, water flux 2,5 mℓ/cm^2.min, pH 1-11,5, operating pressure 3,74 bar, maximum temperature ≤ 80 °C) and flat sheet membranes (Berghof, BM 500, cut-off 50 000, water flux 0,5 – 1 mℓ/cm^2/min, pH 2 - 12, operating pressure range 0,34 - 4,76 bar, maximum temperature ≤ 80 °C) rejections to sulphides of 2% and more than 85% of proteic and colloidal substances were obtained.

Taking into account that 60 – 65% of the initial sulphide remains in the exhausted liquor and that 5 – 10% is lost in the retentate, the quantity of sulphide that is possible to recycle with an UF system is 55-60% (Molinari, 1995).

Another approach reported in the literature was the employment of microfiltration or centrifugation as pre-treatment techniques in order to remove coarse particles and colloidal lime present in the exhausted bath (Marin and Adzet, 1995).

In a recent study (Cassano, Drioloi and Molinari, 1997; Cassano, Drioli and Molinari, 1998) an innovation in the unhairing operation was proposed and tested on a pilot industrial scale. An unhairing enzyme was used reducing the quantity of sulphide from about 10% (with respect to dry skin) of the traditional operation to 1,5%. The enzymatic unhairing was tested on Spanish goat skins and it was combined to the continuous cross-flow UF of the bath (Figure 1(a)). After 100 minutes from the beginning of the unhairing process, the UF was operated by recycling continuously the permeate in the tumbler. The bath coming from the tumbler was previously screened on a course screen to remove and recover the hair detached from the skin and then forwarded to an UF spiral-wound module (Separem MOPSL 4040 U006, Polysulphone, 6,6 m^2, NMWCO 20 kDa, operating pressure range 1 – 6 bar maximum temperature 50 °C, pH 2 – 11, axial flow rate 1,8 – 6 m^3/h). Analytical measurements (Table 2) carried out on the samples withdrawn during UF showed that the concentration of sulphide in the unhairing bath remained almost constant because the membrane allowed its permeation. The organic components (products of degradation of the keratin and of the interfibrillar proteins, fat substances, etc.) were concentrated in the retentate. Treated skins were compared with the control group (skins treated according to traditional processes with lime and sodium sulphide): the results of the chemical and physical analysis carried out on finished leather showed very similar values in the two groups of treated skins.

Table 2: Analytical determination on liquid sample from the unhairing/UF process[a]

Sample	COD (mg/ℓ O_2)	Proteic nitrogen (mg/ℓ)	Sulphide (mg/ℓ)	Oils and fats (mg/ℓ)	Fatty acids (% in extracted oils)	Triglycerides (% in extracted oils)
Initial bath	5 673	278	158	377	93,0	7,0
Final permeate	2 163	116	265	20	-	-
Half-run bath, 70'	11 453	382	177	1 277	96,5	35,0
Half-run retentate	8 727	438	265	600	61,7	38,3
Half-run permeate	2 800	177	231	108	-	-
Final bath, 160'	6 264	368	241	576	52,1	47.5
Final permeate	11 240	550	266	1 300	76,3	23,7
Final retentate	3 160	220	202	86	-	-

[a]Operating conditions: temperature = 30 °C; input pressure = 2,45 – 3,0 bar; output pressure = 1,2 – 1,4 bar; axial flow rate = 3,0 – 3,6 m^3/h; permeate flow rate = 58 - 200 ℓ/h.

The results show that this new approach is more eco-friendly, safer for the workers and produces very little wastewater pollution because hair is not completely degraded. However, its use in the various tanneries requires preliminary pilot testing to adjust the working recipe for obtaining a specific product.

2.2.3 Deliming-bating

In the deliming step the excess of lime is removed from skins using acids and/or acidic salts (Cassano *et al.*, 2001). In the bating the skins are treated with proteolytic enzymes in order to open the fibrous structure of derm to increase the softness of skins.

In order to reduce the polluting load of this operation the exhausted liquor can be treated with UF membranes (Figure 1(a)). A considerable reduction of fatty substances and COD in the permeate could be obtained through this process. This clear solution can be reused for the preparation of new bating baths or as washing water after appropriate testing.

2.2.4 Degreasing

In the degreasing step the excess of natural fat substances is removed from skins. This operation is carried out particularly for sheepskins where the percentage of fat substances on raw weight is about 30 – 40%. The percentage of high quantities of fat can be the origin of undesirable phenomena such as hardness to touch, loss of physical strength, dyeing imperfections and, particularly, repousse (whitish spots that may appear on the tanned skin or on the final product) (Cassano *et al.*, 2001).

Organic solvents are today the most widely used products in degreasing. They produce a considerable increase in environmental pollution by emission of volatile compounds. Furthermore, they can give problems in biological treatment plants where wastewaters are treated.

In previous studies carried out on exhausted degreasing baths, non-cellulosic tubular membranes were used (Cortese and Drioli, 1978). The observed rejection for surfactants was 91%. Simple alkaline cleanings (NaOH at pH 11), followed by cleaning with water at 40 °C, rapidly take the flow rate of UF membranes to its initial value.

Other experiments were carried out using emulsifying agents as degreasing products (Cassano *et al.*, 1997; Cassano *et al.*, 1998; Cassano *et al.*, 1999). Skins were processed in aqueous solution coupling the degreasing step with UF of the bath (Figure 1(a)).

The UF pilot plant was equipped with a Separem MOPSL 4040 U006 module employed also in the unhairing step. Pickled sheepskins from New Zealand were degreased at a temperature not exceeding 52 °C after a preliminary treatment with glutaraldehyde. During the process the bath was continuously ultrafiltered by recycling the permeate in the tumbler.

The proposed methodology permitted to concentrate, in the feed tank of the UF plant, fat substances removed from the skins. After 300 minutes of UF the concentration factor of oils and fats in the retentate was 4,07. A 55% removal of the initial fat content in the pickled skins was obtained. This value is comparable to that obtained by using a dry-degreasing process with tetrachloro-ethylene. The rejection of the membrane to COD and fatty substances with references to the initial feed was about 95%.

Studies of membrane module cleaning, by using two solutions of Sepaclean (AL-1 and EZ-1 at 1%) showed a good restoration of initial flux using the EZ-1 solution.

The proposed methodology permitted to obtain: -

(a) high removal efficiency of fatty substances from the degreasing bath;

(b) reduction of washing cycles normally employed to remove lipidic substances from skins, and consequently, of water consumption.

These effects were theoretically studied analysing two processes : -

(i) traditional degreasing with continuous supply of fresh water in final washings; and

(ii) degreasing with continuous recycle of permeate from the UF unit.

Theoretical results obtained, assuming several rejection values to oils and fats showed that membranes with a rejection higher than 0,85 have to be used in order to achieve a good removal of fat substances from the bath and a high removal efficiency of fats from the skins (Cassano *et al.*, 2001).

The theoretical model was applied to analyze also the effect of operating parameters on the process performance. For example, by operating with a higher rotation per minute of the tumbler and/or higher recycle flow rates of the permeate, higher $V\infty$ (velocity of the fluid) can be achieved and, thus, higher Km (mass transfer coefficient). This implies that a higher quantity of fats is removed from skins in time obtaining a reduction of the total operating time if transmembrane flow rate is constant.

Depending on the hours of use per day of the UF plant, the pay-back period, as compared to other similar applications, should range between 1 and 4 years. However, more data on the performance of a pilot plant are required for a complete cost analysis.

2.2.5 Pickling

Pickling is an operation of the tanning cycle in which the last residual lime in the skin is eliminated by means of acidification and dehydration of the fibres. These objectives are reached using acid solutions (sulphuric, hydrochloric, formic, lactic) in the presence of adequate salt concentrations (sodium chloride, sodium sulphate and salts of the acid used). Consequently, chromium salts can cross the skin very fast (Cassano *et al.*, 2001).

Conventional cleaning-up treatments are generally not able to reduce chlorides and sulphates of the exhausted pickling solutions to meet the limits required by regulations. The chloride concentration of these solutions is high (9 g/ℓ) and also represents a considerable problem for the biological plants.

The osmotic pressure of the exhausted baths is expected to be 12 – 15 bar, so that reverse osmosis could be employed for treatment of the exhausted liquor coming from the pickling, after an appropriate pre-treatment, in order to recover the salt component in the retentate (Figure 1(a)). The recovered solution could be reused in the pickle after adjustment of the salt concentration to optimal level. The permeate solution could be employed for the preparation of the soaking baths or as washing water.

2.2.6 Chromium recovery

In the tannage operation the skin is treated with substances (chromium salts, vegetable substances, aldehydes, oils, etc.) preventing its putrefaction (Cassano *et al.*, 2001).

Chromium basic sulphate is the most widely used tanning substance today. The exhausted bath coming from chromium tannage contains about 30% of the initial salt and is normally sent to a cleaning-up plant. Here chromium salts end up in the sludges creating serious problems for their disposal (Gauglhober, 1986).

Chromium recovery from tanning exhausted baths represents a significant economical advantage for the leather industry in terms of its reuse and for the simplification of the polishing process of global wastewaters.

The traditional methods for chromium recovery is based on the precipitation of chromium salt with caustic soda followed by the dissolution of the chromium hydroxide ($Cr(OH)_3$) in sulphuric acid (Simoncini and Tomaselli, 1977; Technical Brochure, 1992). However, the quality of the recovered solutions is not always optimal as a result of the presence of metals, lipidic substances and other impurities.

In order to improve the quality of the recycled chromium an alternative method using membrane processes was studied (Cassano *et al.* 1997; Cassano *et al.*, 1996; Cassano *et al.* 1999). Types of membranes, operating pressures, temperatures and cleaning conditions were established in preliminary tests carried out on flat sheet membranes. The results obtained in these preliminary tests were used to carry out experiments on pilot scale (Figure 1(b)).

In the first step a chromium solution with an initial concentration of 4 343 mg/ℓ as Cr^{3+} was processed in a pilot plant equipped with an UF spiral wound module (Osmonics 411 TA, PVDF, NMWCO 15-25 kDA, 3 m², maximum pressure 3,8 bar, maximum temperature 45 °C, pH 2-11, water permeability 60 ℓ/m².h.bar). The UF membrane produced a strong reduction of suspended solid components and fat substances, giving rejections of 84 and 98%, respectively, with reference to the initial feed. About 40% of the organic nitrogen was retained by the membrane while the rejection for chromium was 28% (Fabiani *et al.*, 1996).

In order to obtain a tanning or retanning solution the permeate coming from the UF was processed in a pilot plant equipped with a NF spiral-wound module (Separem MOCD 4040 N50, Polyamide, 5,5 m², NMWCO 150 Da, maximum pressure 28 bar, maximum temperature 50 °C, pH operating range 2-11, axial flow rate 1 200 – 4 500 ℓ/h, water flux 47,27 ℓ/m².h).

Nanofiltration (NF) tests were carried out at a temperature of 25 °C, an applied pressure of 14 bar and an axial feed flow rate of 2 200 ℓ/h.

Operating in a concentration operating mode (recycling the retentate continuously and drawing of the permeate) the initial feed volume was reduced until a VRF (volume reduction factor = initial volume divided by the remaining volume) of 3,24.

Analytical measurements (Table 3) carried out on samples coming from the experimental tests showed a very low chromium concentration in the permeate: the membrane rejection versus this component was 99,9%. The concentration of chromium and COD in the retentate and permeate as a function of time is shown in Figure 2. The organic substances (as COD) were less retained with respect to chromium as shown by the increased concentration ratio of chromium/COD in the retentate.

Table 3 : Analytical determinations on samples from ultrafiltration and nanofiltration tests

Parameter	Feed ultra-filtration	Final retentate ultra-filtration	Final permeate ultra-filtration = feed nano-filtration	Final retentate nano-filtration	Final permeate ultra-filtration
pH	3,7	3,7	4,1	4,0	4,0
TSS (mg/ℓ)	612	428	154	370	28
COD (mg/ℓ)	5 960	6 413	5 126	7 641	3 315
Chloride (mg/ℓ)	11 136	11 098	10 844	7 390	13 190
Sulphate (mg/ℓ)	26 137	27 239	27 966	83 455	10 550
Chromium (mg/ℓ)	4 343	5 269	2 729	9 285	30
Ammon. nitrogen (mg/ℓ)	422	420	367	720	320
Organic nitrogen (mg/ℓ)	250	301	165	209	98
Iron (mg/ℓ)	24	29	32	81	8
Calcium (mg/ℓ)	1 100	948	1 086	1 367	12
Manganese (mg/ℓ)	2,2	2,5	2,4	6,3	0,4
Aluminium (mg/ℓ)	91	97	96	259	5
Magnesium (mg/ℓ)	867	822	870	6 162	60
Oils and fats (mg/ℓ)	116	148	-	-	-

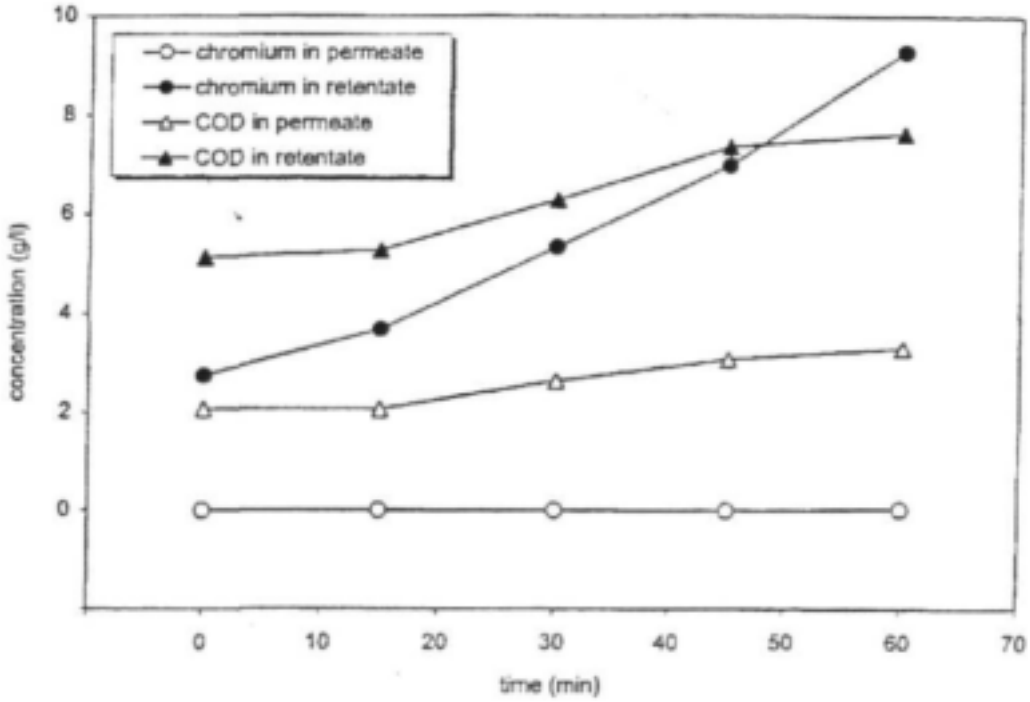


Figure 2: Concentration of chromium and COD vs. time in nanofiltration tests (operating conditions: temperature = 25 °C; applied pressure = 16 bar, axial feed flow rate = 2 200 ℓ/h, permeate flux = 3.63 – 36.0 ℓ/min^2.h) (Cassano *et al.*, 2001)..

A material balance of the NF test using some of the data of Table 3 is shown in Table 4. The balance appears to be good except for COD and TSS: it is probably due to the organic matter adsorption on the NF membrane and plant prefilter. These results agree with those obtained by other authors (Aloy and Vulliermet, 1998).

Table 4 : Material balance on the nanofiltration process

	Initial float	Average filtrate		Final retentate	(%)	Balance (%)
Volume	1 781	1 231	69%	551	31%	100
Chromium	486 g	3,7 g	1%	511 g	105%	106
TSS	27 g	3,4 g	12,6%	20 g	74,1%	86,7
COD	912 g	408 g	45%	420 g	46%	91
Chloride	1 930 g	1 622 g	84%	406 g	21%	105
Sulphate	4 983 g	597 g	12%	4 590 g	92%	104

The chromium concentration obtained in the retentate (1,35% as Cr_2O_3) permits to reuse the solution in the retanning step. A further concentration of the solution using a precipitation-dissolution method permitted to obtained a solution (9,2% as Cr_2O_3) that can be reused as such in the chromium tanning (Figure 2).

Another advantage of the proposed process is the possibility to reuse the permeate in the pickling step considering the high chloride concentrate of this solution.

The recovered chromium solution was used in tanning (after further concentration) and retanning processes. The treated skins were compared with control skins treated with fresh chromium solutions. Chemical and physical analysis (tensile strength, breaking load, elongation at break, shrinkage temperature, etc.) performed on experimental skins revealed values very similar to those obtained on the control group.

A study on membrane cleaning was also carried out after operating the module for chromium recovery in batch type tests for a duration of 3 – 4 hours. Enzymatic (Sepaclean AC-1, 1% v/v) solutions were circulated at 40 °C for about 1 hour or acid solution for 30 minutes at 25 °C . The latter gave a better restoration of the initial water flux as reported in Figure 3.

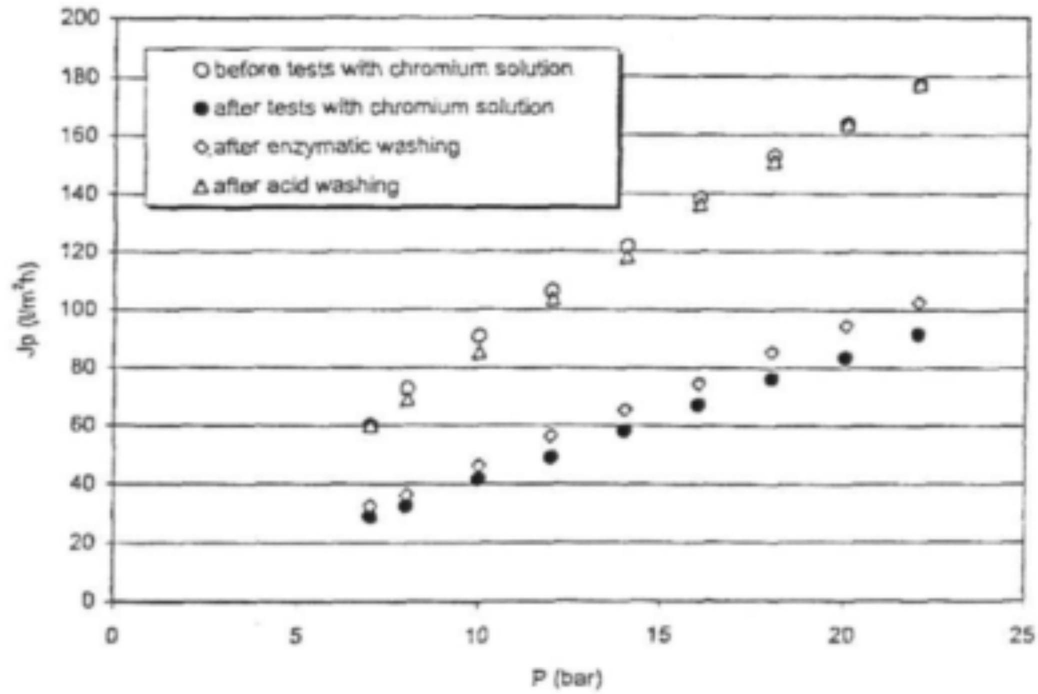


Figure 3 : Effect of membrane cleaning at various applied pressures on water permeate flux (operating conditions: temperature = 25 °C; axial feed flow rate = 2 200 ℓ/h) (Cassano *et al.*,2001)

2.2.7 Vegetable tannage

In the tanning operation the skin is stabilized by using vegetable tannins such as chestnut, mimosa, que brackeo, etc. in aqueous solution (Cassano *et al.*, 2001).

By recycling the exhausted liquor in the feed tank (batch operation mode), it is possible to obtain a concentrated solution that could be reused in the tanning process and a permeate with a low organic content that could be sent to a wastewater treatment plant (Figure 1(b)).

2.2.8 Dyeing

The aim of the dyeing process is to improve the attractiveness of the skins and to increase their commercial value. The skins are treated with dyeing substances in aqueous solution for this purpose (Cassano *et al.*, 2001).

The use of reverse osmosis for recovering hot water, colourants and auxiliaries is an interesting approach already employed in the textile industry (Brandon *et al.*, 1981; Drioli, *et al*, 1976). This process could be successfully applied in the dyeing operation considering that the chemical characteristics of the feed solution are very similar to those measured on the dyeing solutions of the textile industry.

In this sense reverse osmosis could permit to recover dyeing substances in the retentate stream (Figure 1(b)). The permeate solution could be reused as washing water or for the preparation of new dyeing baths.

2.2.9 Wastewater treatment

The cleaning up of tanning effluents usually include the following treatments (Cassano *et al.*, 2001) : -

(a) Primary or chemical-physical treatment (coarse screen, equalization and chemical-physical precipitation with sedimentation and sludge separation);

(b) Secondary or biological treatment with partial or total recycle of sludges and their separation; and

(c) Tertiary treatment (filtration, stripping, redox processes) (Del Pezzo, *et al.* 1980; Peila, 1981).

The biological treatment of tanning wastewater can be coupled to an UF process realizing a membrane bioreactor (Figure 1(c)) that permits cleaning-up, clarification and disinfection (Zenon Environmental, 1995; Brenna, 1997). The bioreactor is constituted by an oxygenated feed tank in which the dissolved organic substances are decomposed by micro-organisms into nitrogen, water and carbon dioxide. The biomass is separated from the effluent by a membrane and recycled in the feed tank. With this treatment high molecular weight substances are rejected by the membrane and they can be further decomposed. The biomass concentration in the system can reach values ten times higher than those obtained in conventional plants.

Another approach is the use of reverse osmosis to reduce the salt content of the final effluent (global wastewaters) produced by tanneries. A modern polishing process (with primary and secondary treatment) permits to reduce most of the polluting parameters (suspended solids, BOD, COD, chromium, sulphides, etc.) to meet the limits required by regulations. Chlorides, sulphates, ammonia, surfactants and solvents often do not fall within these limits.

The final effluent produced by tanneries has a high salt concentration, above the low limits for their discharge in a public sewerage system. Reverse osmosis was tested on wastewater coming from a filter pressing operation (Figure 1 (c)) of chromium (III) hydroxide panels (Cassano *et al.*, 1997; Cassano *et al.*, 1999). A pilot plant equipped with a spiral-wound RO module (Separem MSCB 4040, TFC/polyamide, 6,6 m^2, typical salt rejection 99,2%, maximum pressure 42 bar, maximum temperature 50 °C, pH 4-11 axial feed flow rate 1,5 – 4 m^3/h) was used. The solution was processed at a temperature of 30 °C, an applied pressure of 38 bar and on axial feed flow rate of 2 500 ℓ/h. Analytical determinations on the permeate are shown in Table 5; salt concentration in the permeate showed values below the low limits (Cl^- = 120 – 1 000 mg/ℓ; SO_4^{2-} = 60 – 240 mg/ℓ) with respect to the retentate stream (Figure 4). High salt concentrations in the final retentate suggested its reuse in the pickling step.

Table 5 : Analytical determinations of final permeate from reverse osmosis tests[a]

Parameter	Concentration
pH	8,3
TSS (mg/ℓ)	6
COD (mg/ℓ)	470
Chloride (mg/ℓ)	1 078
Sulphate (mg/ℓ)	167
Chromium (mg/ℓ)	0,4
Ammon. nitrogen (mg/ℓ)	34
Organic nitrogen (mg/ℓ)	24
Iron (mg/ℓ)	3,1
Calcium (mg/ℓ)	6,8
Manganese (mg/ℓ)	0,16
Aluminium (mg/ℓ)	0,81
Magnesium (mg/ℓ)	3,2
Oils and fats (mg/ℓ)	3

[a]Operating conditions : temperature = 30 °C; applied pressure = 38 bar; axial flow rate = 2 500 ℓ/h; permeate flow rate = 12,5 – 72 ℓ/h .

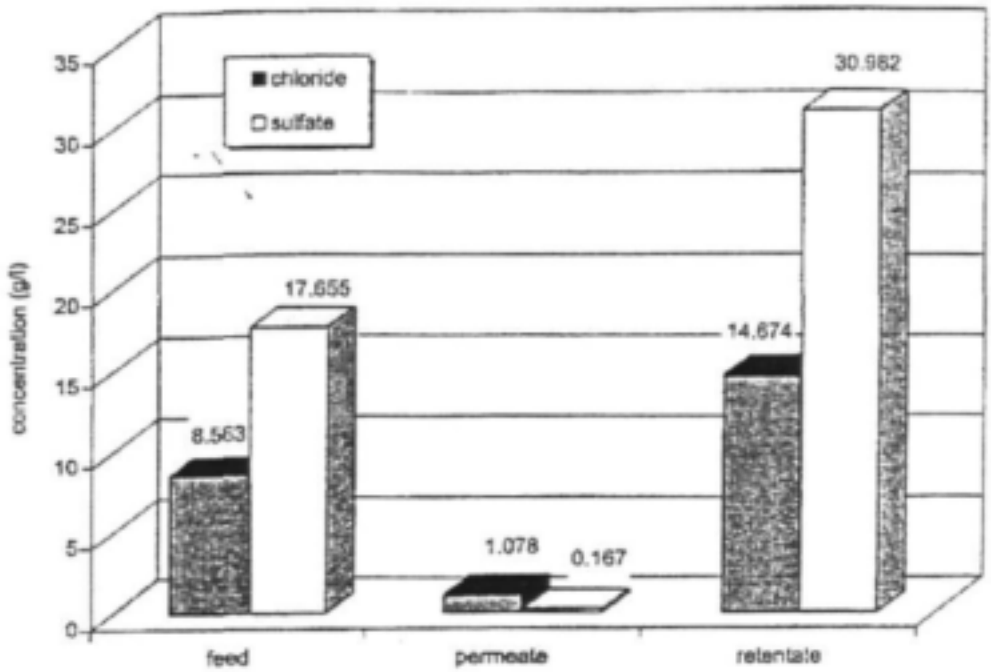


Figure 4: Sulphate and chloride concentrations in reverse osmosis tests on wastewater from filterpressing (operating conditions: temperature = 30 °C; applied pressure = 38 bar; axial feed flow rate = 2 500 ℓ/h; permeate flow rate = 12.5 – 72 ℓ/h) (Cassano *et al.*, 2001).

Chemical and physical analysis carried out on skins treated with the concentrated solutions revealed values very similar to those obtained on control skins pickled with conventional solutions.

2.2.10 Outline of Direct and Indirect Energy Saving

Since membrane operations utilize basic electrical energy, the estimation of the benefit associated to the use of a membrane process as an alternative to a conventional one can be done by applying the 'substitution coefficient' method introduced by 'Electricité de France' in 1981 (Electricité de France, 1981) according to Cassano *et al.*, (2001). This coefficient defined by the ratio between the primary energy (thermal) saved in the process, with respect to the conventional process, and the amount of electrical energy consumed, referring to the conventional process.

In the energetic analysis a leather industry of medium potentiality is considered (Table 6); it is the most representative case of the real situation of this kind of industry. In particular, the developed analysis concerns some operations, previously described, for which a treatment process seems to be more interesting, permitting a significant saving of raw materials and/or reduction of the pollution load in the global wastewater plant.

The cycle steps analyzed for are the following : -

(a) Exhausted bath from a classical unhairing-liming step treated by UF;
(b) Exhausted bath from an enzymatic unhairing-liming step treated by UF;
(c) Exhausted bath from a degreasing step treated by UF;
(d) Exhausted bath from a chromium tanning step treated by a UF/NF integrated process.

Table 6 : Characterization of a typical leather plant considered for the energetic analysis developed

Plant potentiality ($kg_{leather}$/cycle)	12 000
Number of whole treatment cycles for a week	3
Number of working weeks for a year	45
Number of working days for a week	5
Annual plant potentiality ($kg_{leather}$/year)	1 620 000
Daily plant potentiality ($kg_{leather}$/day)	7 200

(a) Classical unhairing-liming step integrated with UF

The unhairing-liming treatment using sulphides (Molinari, 1995) requires, for each kilogram of treated leather, a consumption of about 0,012 kg of sulphides (62% purity), 0,01 kg of auxiliary products and 0,003 m^3 of water. Twenty percent of the utilized sulphides are consumed by the unhairing treatment; 15 – 20% is adsorbed on the leather; thus the residual sulphides in the exhausted bath are 60 – 65% of the initial load (Vulliermet, 1980). Assuming for the UF step (characterized by a membrane rejection to sulphides of about 2%) a loss of 5 – 10% in the retentate stream, the amount of sulphide that is possible to recover with a UF system is about 55 – 60%. The possible recovery of water is about 70%.

The classical unhairing-liming treatment, integrated with the membrane system, permits to reach some benefits related to significant saving of chemicals (sulphides and auxiliary products) and water and to the reduction of the wastewater treatment problems (COD reduction of about 30 – 35% in the global waste) by degreasing organic and inorganic substances concentration in the exhausted bath.

The results of the energetic analysis are summarized in Table 7.

Table 7: Energetic analysis results for the unhairing-liming treatment using sulphide integrated with a membrane operation (UF)

Benefits (EUR/year)	38 653,7
Sulphide saving	14 725,2
Auxiliary products saving	2 284,1
Water saving	21 691,2
Waste treatment cost saving	4 183,3
Recovery proteins	
Costs (EUR/year)	722,9
Electrical energy	38 734,3
Plants investment	309,9
Pretreatment	4 067,1
Work	826,3
Chemicals	3 615,2
Maintenance	
	33 261,9
Economical balance (EUR/year)	358,9
Primary energy saving (GJ/year)	
	51,3
Total substitution coefficient (MJ/kWh)	

(b) Enzymatic unhairing-liming step integrated with UF

It is interesting to estimate if there is an economical and energetic benefit using, instead of a classical unhairing-liming operation, integrated by membranes, a recovery system represented by an enzymatic treatment combined with a UF plant. This solution allows to obtain both a sensitive reduction of sulphides (and auxiliary compounds) consumption in the bath, by a partial substitution of these chemicals with a relatively small amount of enzyme (about 1% with respect to the weight of dry leather treated), and chemicals recovery in the permeate stream (about 55 – 60%). Then, the sulphide saving considered in the analysis includes not only the reagent recovered by UF but also the amount of this chemical substituted by the enzymes.

The results of the energy analysis, which is relative to an UF plant characterized by the same potentiality of the one considered in the previous evaluations, are shown in Table 8.

Table 8: **Energetic analysis results for the unhairing-liming treatment using enzymes integrated with a membrane operation (UF).**

Benefits (EUR/year)	63 954,3
Sulphide saving	143 236,2
Auxiliary products saving	2 284,1
Water saving	43 382,4
Waste treatment cost saving	5 019,9
Recovery proteins	
Costs (EUR/year)	722,9
Electrical energy	38 734,3
Plants investment	309,9
Pretreatment	4 067,1
Work	826,3
Chemicals	3 615,2
Maintenance	4 183,3
Enzymes	
	209 601,3
Economical balance (EUR/year)	2 261,9
Primary energy saving (GJ/year)	
	323,2
Total substitution coefficient (MJ/kWh)	

(c) Degreasing step integrated with UF

A typical degreasing step requires the consumption of about 0,5 g of surfactants for each kilogram of treated leather. Using a UF plant to treat the exhausted bath from the degreasing operation, it is possible to obtain, as verified by experimental tests, a good recovery of surfactants. The surfactants could be recycled to the degreasing step with raw materials cost reduction; furthermore, the reuse of fatty components from the retentate stream after some chemical and physical treatments, in the fat liquoring step, can give a drastic reduction of the wastewater treatment costs (Table 9).

Table 9: Energetic analysis results for the degreasing treatment integrated with a membrane operation (UF)

Benefits (EUR/year)	817,8
Surfactants saving	3 480,5
Water saving	36 152
Waste treatment cost saving	836,7
Greases recovery	
Costs (EUR/year)	771,1
Electrical energy	23 240,6
Plants investment	247,9
Pretreatment	4 067,1
Work	495,8
Chemicals	2 169,1
Maintenance	
	10 295,4
Economical balance (EUR/year)	111,1
Primary energy saving (GJ/year)	
	18,9
Total substitution coefficient (MJ/kWh)	

(d) Chromium tanning steps integrated with membrane operations (UF &NF)

The chromium recovery from exhausted baths of tannage is a significant advantage, both in terms of its reuse and for the simplification of the global wastewater cleaning-up processes. The result from an economic and energetic analysis of the tanning process integrated with membrane operations show that low energy and low investment costs are required if compared to the process without any recovery (Table 10).

Table 10: Energetic analysis for chromium recovery by integrated membrane operations (UF + NF)

Benefits (EUR/year)	1 144,2
Chloride saving	3 355,9
Chromium saving	587,3
Water saving	43 382,4
Waste treatment cost saving	
Costs (EUR/year)	614,4
Electrical energy	25 822,8
Plants investment	309,9
Pretreatment	4 067,1
Work	826,3
Chemicals	3 615,2
Maintenance	
	13 214,03
Economical balance (EUR/year)	142,6
Primary energy saving (GJ/year)	
	23,98
Total substitution coefficient (MJ/kWh)	

However, to verify the opportunity to substitute the traditional recovery process with a membrane operation, it is necessary to carry out an analogue energy analysis for the first one, to compare their 'total substitution coefficients.'

The results of the energetic analysis are summarized in Table 11.

Considering that 1 kWh of electrical energy, available at the utilization site, requires in a power station 10,5 MJ of primary energy from combustion, the process innovation results are good when the substitution coefficient is greater than 10,5 MJ/kWh (Molinari *et al.*, 1995). As shown in Table 11, all new membrane process solutions analyzed are energetically acceptable.

Table 11 : Summary of energetic analyses for the studied tanning processes

	Primary energy saving (GJ/year)	Total substitution coefficient (MJ/kWh)
Unhairing-liming treatment		
Using sulphide integrated with a membrane operation (UF)	358,9	51,3
Using enzymes integrated with a membrane operation (UF)	2 261,9	323,2
Degreasing treatment integrated with a membrane operation (UF)	111,1	18,9
Chromium recovery process with membrane operations (UF + NF)	142,6	23,98

2.2.11 Conclusions

The presented applications of pressure driven membrane processes in the various wet operation steps of the leather industry can result in clean chemical operations. The experimental results obtained in small-scale pilot plants on liming,
tannage show the possibility to realize into more efficient operations to recover by-products (e.g. proteins and fats) and chemicals (e.g. chromium). The proposed new applications of membrane operations in soaking, deliming-bating, pickling, vegetable tannage and dyeing steps can further increase the advantages already described for the experimental cases. The energy analysis shows an advantage from an energetic point of view.

The application of membrane processes integrated in some steps of the tanning cycle could be employed in the future in the plant innovation phase of the leather industry (excluding sulphide recovery and recycle which is already used in some tanneries). However, further research is needed case by case to adopt and optimize a specific modification to the proper factory working cycle. A careful study of the type of pretreatment needed for each exhausted bath is also required.

The general advantages obtained in the rationalization of the operating steps of leather manufacture are the recovery and reuse of primary resources. This produces reduction of environmental impact, simplification of polishing processes of wastewaters, easy reuse of sludges, decrease of disposal costs, savings of chemicals and water, saving of direct and indirect energy. The described applications confirm the new important possibilities of having for this industrial sector a sustainable growth also in the industrialized countries.

3. PROGRESS REPORT ON THE OPERATION OF A PILOT RO UNIT AT ATH TANNERY, MELVISHARAM, INDIA

3.1 INTRODUCTION

Emmanuel (1999) has described the operation of an RO pilot plant for the treatment of the final effluent produced by a tannery in India. The tannery industry in India, particularly in the Vellore District of Tamil Nadu, is facing the problem of disposal of treated effluent containing a high concentration of TDS. As part of its efforts to find a viable method of dealing with the TDS problem, UNIDO established a pilot RO unit at ATH tannery, Melvisharam in collaboration with M/S Aqua Chemicals and Systems Ltd., Chennai. The system was initially established in April 1998 and operated until the end of December 1998. The performance details of this unit for the first six months operation period was presented in a report titled 'Report on Performance of a pilot reverse osmosis unit installed at ATH tannery,' submitted in the month of December, 1998.

The operation of the pilot plant was extended for another six months primarily to accurately evaluate the cost-efficiency of the system and the behaviour of the membranes in RO-1 and RO-2. Though one year is too short a period to ascertain the longevity of the membrane, yet the performance of the system at the end of one year should definitely give an indication of the health of the membranes. Also, essential pre-treatment requirements of the system should be established at the end of this period.

This part provides performance details of the unit during the period December 1998 to March, 1999 (Emmanuel, 1999).

3.2 OPERATION DETAILS OF THE UNIT

3.2.1 December, 1998

The unit was operated until the third week of December with the following operating conditions : -

- Operation time : 9.30 a.m. to 5.30 p.m.; Feed capacity : 8 m^3/day.
- Once a day of back washing of pressure filter (MGF) and activated carbon filter (ACF) as well as regeneration of the softener. Replacement of cartridges in cartridge filter was done once in fifteen days.
- Pressure in RO-1 : 9 – 11.5 kg/cm^2 (reach the maximum by the evening).
- Pressure in RO-2 : 14 – 17.5 kg/cm^2 (reach the maximum by the evening).
- TDS : Raw water : 4 000 mg/ℓ - 5 500 mg/ℓ, Permeate : 100-220 mg/ℓ and

Reject : 9 000 – 25 000 mg/ℓ (the lower and higher values mentioned for permeate and reject were the one in the morning and in the evening).

- Dosage of chemicals – hydrogen peroxide : nil, hydrochloric acid : 6 – 10 mg/ℓ, antiscalant : 10 mg/ℓ, antioxidant : 10 mg/ℓ .
- Average daily power consumption was around 40 kWh.
  Flow pattern : Feed : 8,3 m^3/day, permeate : 6,5 m^3/day, reject : 1,15 m^3/day, others (washings) : 0,5 m^3/day, Yield : 70 – 80%.

By the third week of December, 1998, the colour of the treated effluent had shown a sudden increase following the application of a red dye which was not commonly used in the tannery. The effluent treatment plant (ETP), being not accustomed to this dye, could not remove it, leading to the entire ETP including aeration tank becoming red in colour.

The company operating the pilot RO unit contemplated temporary shutdown of the plant until restoration of the normal condition. However, finally they decided to continue the operation on the following considerations : -

(1) The tannery could not give a categorical statement when the usage of red dye will be stopped.

(2) It was earlier planned to run the pilot RO unit until December, 1999. It was therefore considered to take the risk, mainly to determine the adverse effects if any, of the red dye.

Ideally, the pretreatment provided as a part of the system i.e., photochemical oxidation would have taken care of the system by oxidising the red dye. However, dosing of hydrogen peroxide which was originally provided was suspended following the oxidation of sealant in RO-2 during May, 1998.

However, due to the adverse effect of the red dye, the nanofilter membrane got clogged and after cleaning with cleaning solutions, the operation had continued from 25 December 1998 onwards.

From 25th December onwards, the operation mode was changed to 24 hour continuous operation instead of the previous 8 hour operation per day.

3.2.2 During January, 1999

During January, 1999, the system was operated continuously, average operating period excluding the time spent on backwash and regeneration was 18 – 20 hours a day.

Operational aspects during January, 99 were as follows : -

(1) No dosage of hydrogen peroxide in the photochemical oxidiser was done.

(2) Backwashing of pressure filter (MGF) and activated carbon filter (ACF) as well as regeneration of the softener was done 2 – 3 times every day. In general, the backwashing frequency increased.

(3) Replacement of cartridges in the cartridge filter was done once in 3 – 4 days. This frequency also had increased, mainly due to high suspended solids in the treated effluent from the tannery ETP.

(4) The online conductivity meter had gone out of order and was replaced after repair by the end of January, 1999. The period of operation when the meter was not functioning (around 15 days) was not considered as a part of extended six months operation.

(5) Pressure in RO-1 : 14 bar, Pressure in RO-2 : 19 bar, Raw water TDS : 5 500 – 6 800 mg/ℓ, Final TDS in permeate : 350 – 550 mg/ℓ, Reject TDS : 26 000 – 28 000 mg/ℓ .

(6) Dosage of chemicals – hydrogen peroxide : nil, hydrochloric acid : 8 – 10 mg/ℓ, antiscalant : 20 mg/ℓ, antioxidant : 20 mg/ℓ .

(7) Power consumption : 148 units (kWh) per day (average).

(8) Flow pattern : Feed : 1,1 m^3/hr, permeate : 0,9 m^3/hr, reject : 0,12 m^3/hr, & washings: 0,08 m^3/hr, Yield : 70 – 80%.

3.2.3 February, 1999

The continuous operation of the system was continued until 5 February, 1999 and thereafter the operation pattern was restored to 8 hours operation. The salient operation features are given below: -

- Operating time : 8 hours a day
- Frequency of cartridge replacement in cartridge filter : once in 7 days
- Backwashing frequency : Pressure filter (MGF), Activated carbon filter (ACF) and regeneration of the softener : once a day. Only freshly treated effluent is used for backwashing from 20 February 1999 for backwashing.
- Pressure levels – RO-1 : 18 bar, RO-2 : 19 bar
- TDS levels – Raw water : 4 800 – 6 200 mg/ℓ, Permeate : 300 – 350 mg/ℓ, Reject : 21 000 – 24 000 mg/ℓ
- Dosage of chemicals – Hydrogen peroxide : nil, Hydrochloric acid : 8 – 10 mg/ℓ, Antiscalant : 20 mg/ℓ, Antioxidant : 20 mg/ℓ
- Power consumption – 51 units (kWh) per day (average).

- Flow pattern : Feed : 1.1 m^3/h, permeate : 0.9 m^3/h, reject & washings : 0.1 – 0.2 m^3/h, Yield : 70 – 80%.

The performance of the nanofilter progressively deteriorated during February, 1999 and the pressure in the nanofilter started going up to 19 – 20 bars in the evening. The nano pump broke down during February 1999 due to higher than allowed pressure (20 bars). Following this, a meeting of ACS in the presence of Scientists from CLRI was called by Mr A Sahasranaman, Programme Coordinator of RePO. The minutes of the meeting are given in Annex-1. As decided during the meeting, a thorough inspection of the pilot RO unit was carried out by the Director of ACS in presence of representatives from RePO and CLRI and detailed recommendations were made. The inspection report is given in Annexure 2.

3.2.4 March, 1999

As mentioned earlier, attempts to maintain the designed permeate rate from RO-1 (nanofilter) had resulted in a pressure build-up in the filter and shut down of the system. In order to keep the system operating, the flow pattern was redesigned, so as to have 1.2 m^3/hr permeate flow from RO-1 as against a designed flow rate of 1.7 m^3/hr. Due to the low recovery from the nanofilter, the feed to the RO-2 unit has come down and to overcome this imbalance, the nanofilter was re-designed to operate for 12 hours so as to provide input for RO-2 for 8 hours.

The operational aspects during March are given below : -

- Operation of units up to the nanofilter (RO-1) was done for 12 hours (from 08.00 hrs to 20.00 hrs) and operation of RO-2 unit was done for 8 hours in 3 intervals (i.e., 10 – 13 hrs; 15 – 14 hrs; 19 – 21 hrs).

- Backwashing – pressure filter (MGF), activated carbon filter (ACF) and regeneration of softener: once a day. Only freshly treated effluent was used for backwashing.

- Replacement of cartridges in cartridge filter : once in 6 days.

- Pressure in RO units – RO-1 : 13 – 14 bar (for low recovery), Pressure in RO-2 : 19 bar.

- TDS – Raw water : 4 200 – 6 300 mg/ℓ, Permeate : 300 – 450 mg/ℓ, Reject : 21 000 – 26 000 mg/ℓ

- Dosage of chemicals : Hydrogen peroxide : nil, Hydrochloric acid : 8 – 10 mg/ℓ, Antiscalant : 20 mg/ℓ, Antioxidant : 20 mg/ℓ .

- Power consumption : 57 units (kWh) per day (average).

- Flow pattern : Feed : 8,5 m^3/d, permeate : 6,3 m^3/d, reject & washings : 2.2 m^3/d, Yield : 70 – 75%.

  The same operational features were maintained until the end of March, 1999.

3.2.5 Cost of Operation

(a) During 8 hours per day operation

The average cost of operation observed during the three months period when 8 hours operation was carried out per day was as follows : -

Power cost : 50 units (kWh) per day = Rs. 205
Chemical cost/day including salt for the softener regeneration : Rs. 48
Labour cost (two operators)/day = Rs. 110,
Total = Rs. 363 per day
Average quantity of effluent treated = 8.53 m^3
Average quantity of water recovered per day = 6.73 m^3.

Cost of cubic meter of effluent treated = Rs 42.55 = US $ 1.01
Cost of recovered water per cubic meter = 53.9 = US $ 1.26

(b) During 24 hour operation

Power cost per day : 138 units (kWh) per day = Rs. 567
Chemical cost/day including salt for the softener regeneration : Rs. 105.6
Labour cost (three operator)/day Rs. 165,
Total = Rs. 837 per day.
Average quantity of effluent treated = 20.9 m^3
Average quantity of water recovered per day = 17.1 m^3

Cost of cubic meter of effluent treated = Rs 40.04 = US $ 0.94
Cost per cubic meter of recovered water = 48.9 = US $ 1.15

It is assumed that the operation cost would be lower for higher capacity units.

3.2.6 Other modifications

The following additional modifications were done on the operation of the unit during the period December 98 – March 99.

(1) Earlier, the rejects were directly discharged to a line leading to solar evaporation pans for disposal. A flow meter cum totaliser was installed in the line. However, it

was noted that this flow measurement was not very accurate. The manufacturer of the flow meter explained that the problem was due to the very low flow rate through the line. This necessitated an alternate arrangement for flow measurement. Further, there was no online measurement for other rejects, such as rejects from the softener, etc. Hence an arrangement for collection of all reject water for quantity assessment as well as a composite sampling was considered and a concrete tank of size 2.0 meter diameter and 2 meter depth which was lying idle near the new tannery shed, was used. From end of February, 99 the measurements as well as sampling were done using this tank.

(2) The suspended solids concentration as well as the colour of the effluent remained high after the incidence of the red dye. To improve the performance of the ETP, a tertiary chemical treatment was planned. Tests in the laboratory were conducted to determine the optimum chemical dosages to improve the performance of the ETP. Chemical dosing using 200 mg/ℓ lime as a tertiary treatment was found to reduce the suspended solids, and this chemical dosing started regularly in the ETP from end of February.

(3) The pilot RO unit has been designed to treat TDS in the range of around 8 000 mg/ℓ . However, since the processing of raw hides is seldom done in the tannery, this designed TDS could not be given to the inlet of pilot RO unit. Hence, it was considered to bring some high TDS treated effluent from outside and mix it with the treated effluent from ATH tannery so as to make the combined TDS in the inlet to 8 000 mg/ℓ. The treated effluent from Vishtec CETP, Melvisharam was considered ideal for the purpose due to the following reasons: (1) The TDS in the effluent is fairly high (up to 11 000 mg/ℓ) and the other parameters of the treated effluent such as BOD, COD, TSS etc. are comparable to those of the ATH effluent. (2) The CETP is close to the tannery and transportation of the effluent would be easy. Consequently, the old aeration tank of the ETP with a storage capacity of 100 m^3 has been cleaned and modified to use as a treated effluent collection tank to facilitate continuous feeding of the system with mixed treated effluent from Vishtec and ATH in the ratio 1:1. The supernatant from the chrome recovery unit was considered earlier for addition with the treated effluent to increase the TDS, but the large amount of suspended solids and sulphates in the CRU supernatant prevented adoption of this course. This trial, however, would only be done after replacement of the nano membranes.

(4) Disposal of rejects from the RO unit is the principal technical problem in operation of an RO unit for the treatment of tannery effluent. It was stated that since the RO rejects are free from suspended solids and other organics, it would evaporate faster and the dried up salt could be used in some application, as it would be purer compared to the salt obtained from solar evaporation tanks. Hence, evaporation studies were carried out to find the rate of evaporation and purity of evaporated material. Since the volume of solar evaporation tanks available in the tannery is

much more than the small volume discharged from the pilot RO unit, segregated loading of the solar evaporation tank with rejects from the RO was found difficult. Hence, a sludge drying bed lying adjacent to the pilot RO unit was emptied and made impervious by laying LDPE sheets. The evaporation of rejects from RO-1 and RO-2 was carried out in this makeshift tank. The average evaporation rate was observed to be 8 mm/day for a liquid depth of 30 – 50 mm. The salt obtained from reject from RO-1 was brownish with mostly sulphates as major component. The salt obtained from RO-2 reject was pure transparent crystal with more than 95% pure sodium chloride.

3.2.7 Future course of action

The replacement of the nano membrane was expected to be completed by mid May, 1999. Once the nano membranes were replaced, the trial with designed TDS of 8 000 mg/ℓ would be taken up. Thereafter the operation would mainly focus on : -

(1) Finalisation of a proper pre-treatment system for future RO units.
(2) Optimising dosages of chemicals for pre-treatment and short listing suitable chemicals for colour/COD removal for tertiary treatment of the effluent to remove harmful contaminants (such as the red dye), etc. in the effluent.
(3) Preparation of emergency plans giving details of precautions to be taken for abnormal operational conditions.
(4) Assessing optimum recovery possible in the pilot unit.
(5) Actual cost of operation and projected cost for a large-scale operation.

3.2.8 Conclusion

The operation of the pilot unit during the period December, 1998 to April, 1999 was some what affected by the red dye problem. However, this incident provided some lessons concerning the possibility of damage to the system due to such an accident. The remedial and preventive measurements against such risks would be integrated into the future designs.

The evaporation studies provided useful information which would have greater relevance in programming disposal of concentrated liquor from RO systems, considered today as the biggest technical difficulty. Studies involving utilization of RO-2 reject in pickling process also should provide useful information on the management of rejects.

4. ULTRAFILTRATION FOR COLOUR REMOVAL OF TANNERY DYEING WASTEWATERS

4.1 Introduction

Ives and de Pinho (2000) have described UF for colour removal from tannery dyeing wastewater. Dyeing is one of the polishing operations which is performed after the leather is greased in order to better receive the dyestuff. The low efficiency of the process leads to large amounts of greases and dyes which are not consumed in the process and cause highly polluted and strongly coloured wastewaters.

In the dyeing of wastewaters of the tannery industry the dyes are associated with large amounts of grease, and therefore UF would be more efficient than RO to remove the dyes bound to the fat and achieve colour removal. The resulting streams of the UF process are a concentrate of fats and dyes and a permeate containing water and small amounts of dyes and salts. UF was evaluated in terms of productivity and quality of permeate water in this study as a function of the membrane molecular weight cut-off and operating conditions.

4.2 Conclusions

Ultrafiltration is a suitable process to decolourize the wastewaters coming from the dyeing cycle of the tannery industry because the dyes are bound to fat and adsorptive fouling occurs, which allows for the retention of low molecular weights solutes such as dyes. The colour of the permeate waters depends on the membrane and on the effluent used. Rejection was always above 70%, meaning that there is a possibility of using these waters as process waters in other baths. This would to be investigated in future work. In any event, these wastewaters can always be used in the next leather washing steps after the dyeing operation.

Discharge is possible when a dilution of 1:20 results in water with an absorbance equal to pure water. This is true for the cases of colour rejections above 95%, namely membranes with 5 and 3 kDa MWCO facing effluents E1 (pH 2,8; Conductivity, mS/cm 23,0; TSS, mg/ℓ 25,9; TS g/ℓ 56,0; Colour, g/ℓ 5,1) and E3 (pH 3,2; Conductivity 13,8 mS/m; TS, g/ℓ 39,3; Colour, g/ℓ 38,7). However, discharging is not the main goal if the waters can be reused for other purposes, which is the case.

In both types of operating modes (CLR or B), there is a severe decline of the permeate fluxes with respect to the corresponding pure water fluxes. This is due to the severe fouling characteristics of the effluents, and this effect is particularly acute for high MWCO membranes. In fact, for two different effluents (E1; E1: pH 2,8; Conductivity, mS/m 23,0; TSS, mg/ℓ 25,9; TS, g/ℓ 56,0; Colour, g/ℓ 5,1) and E2; E2: pH 3,5; Conductivity, mS/cm 15,4; TSS, g/ℓ 19,0; TS, g/ℓ 28,0; Colour, g/ℓ 31,0), the permeation flux displayed by the membrane of 40 kDa is very low compared with those of membranes of 10 or even 5 kDa. High-MWCO membranes thus show low performances in terms of both colour rejection and productivity rates.

The influence of the nature of the effluents in the separation process is also evident in terms of colour rejections. Also for both modes of operation, effluent E1 shows a colour rejection around 75%, independently of the membrane used (10 or 40 kDa). For the other two effluents, E2 and E3, colour rejections are much higher, thus showing a weak influence of the membrane used. This effect is also in great evidence when, for example, the performance of the same membrane of 40 kDa facing effluents E1 and E2 is compared: colour rejections are much higher for effluent E2.

The most tight membranes of 5 and 3 kDa present, at the same time, show high fluxes and high colour rejections.

UF experiments made under different conditions of applied pressures and Reynolds numbers for the 3 and 5 kDa membranes, show that for both membranes there is an improvement of the permeation fluxes at the highest Reynolds numbers of 9 800 and 13 900, meaning, therefore, the minimization of concentration polarization effects.

As far as the pressure effect goes, one sees that for the 5 kDa membrane the apparent rejection to colour increases when the pressure increases, and this effect is more pronounced for the lower Reynolds number, meaning the occurrence of adsorptive fouling. In fact, for this Reynolds number the overall rejections are higher than for the pressure range. For the 3 kDa membrane the colour rejections are practically independent of the pressure and of the Reynolds number.

Concentration polarization and adsorptive fouling both occur and are dependent on the operating conditions. They are minimized at the pressure of 1.5 bar and at the highest feed circulation rates.

Finally, rejection of total solids is low for all the membranes and effluents under study and for a VRF of 10.

5. CHROMIUM (III) SALTS RECOVERY PROCESS FROM TANNERY WASTEWATERS

5.1 INTRODUCTION

Fabiani *et al.* (1996) have described a chromium (III) salt recovery process from tannery wastewater. Chromium (III) salts and sulphur compounds are the main pollutants released in tannery wastewaters and in the atmosphere. Wastewater treatment plants produce more than 700 000 ton/y of sludges and residues in Italy. Treatment and disposal costs amount to about 840 000 Mlir/y (560 Mlir equals 1 US $). The impressive dimension of this environmental problem pushes to transfer in tanneries any available technological improvement to reduce the environmental impact, and to recover and recycle water and the main chemicals. Consequently, an improvement of the chromium recovery cycle by means of membrane processes was evaluated as well as some of the environmental and economic benefits.

5.2 CONCLUSIONS

Chromium (III) salts are the most widely used chemicals for tanning processes, but only 60% of the total chromium salt reacts with the hides. Therefore, about 40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions). The presence of chromium (III) and salts in the sludges of both the wastewater biological treatment plants or the chemical plants for recycling spent tanning liquors, represents an inconvenience for the safe reuse of these sludges and a cost forming factor for their disposal. Among the several proposed methods for chromium recovery, lime or sodium hydroxide precipitation and filter-pressing of the chromium hydroxide is the usual way to recover chromium salts from spent process solutions or from leaching solutions of residues of hides. However, usually the chromium salt quality must be improved for their reuse in tanning processes. The integration of membranes in the treatment process for chromium recovery reduces the environmental impact, favours the reuse of both the protein residue and the biological plant sludges, reduces the consumption of chemicals and decreases the costs of waste disposal.

The actual management of the chromium exhausted bath for metal recovery and reuse in the tanning process allows to reach a high recovery yield of chromium. However, the quality of the salt is depleted because of the presence of organic matter. Moreover, the recovery process produces a lot of sludges especially in the flocculation and finishing steps. The use of chemicals for pH control, precipitation and acid dissolution of chromium hydroxide also contribute to the process costs.

The proposed process on the contrary allows a recovery of chromium in solution at a level of 28% while the presence of organic matter is low suggesting the possibility of a direct concentration of the obtained solution or its use to make up new tanning bath with addition of chromium salt. These results could be achieved with direct ultrafiltration of the waste solution at expenses of the permeate flow which is very low because of the membrane clogging due to the presence of suspended solids, oils and fats. Low permeate flow means large membrane area and high investment costs. The coupling of a microfiltration pretreatment of the waste solution with ultrafiltration produces a clean chromium salt (permeate) solution and allows at the same time to work with fluxes four-five times higher reducing the membrane area needed for ultrafiltration.

According to the proposed process, a reduction of the sludges produced is expected which means a saving in the chromium recovery process costs.

6 EFFECTIVE MANAGEMENT OF SULPHUR AND CHROME COMPOUNDS

6.1 INTRODUCTION

To meet the requirements of reducing the salt content of wastewater, a study was undertaken about the feasibility of removing salt by means of solar evaporation and by membrane technologies like : ultrafiltration, reverse osmosis and electrodialysis as well as the decontamination of recovered salt (Langerwerf, *et al.*, 1998).

6.2 CONCLUSIONS

Desalination by means of membrane technologies turned out to be very expensive. The concentrated brines constitute a new problem as almost no application is available to treat these concentrates effectively. However, it is claimed that the dual cell electrodialysis of spent chrome liquor offers possibilities for the useful application of the resulting concentrates and diluates. In this case the first cell is fed with salt-contaminated groundwater. It produces desalted water applicable in the tannery and a salt-enriched stream to be used as stripping liquor in the second cell. The second cell is fed with spent chrome liquor and it produces a nearly chrome-free sulphate liquor to be used as pickle solvent, and a chrome liquor with an adequately reduced sulphate content, to be used as the main chrome tanning solvent (Figure 5).

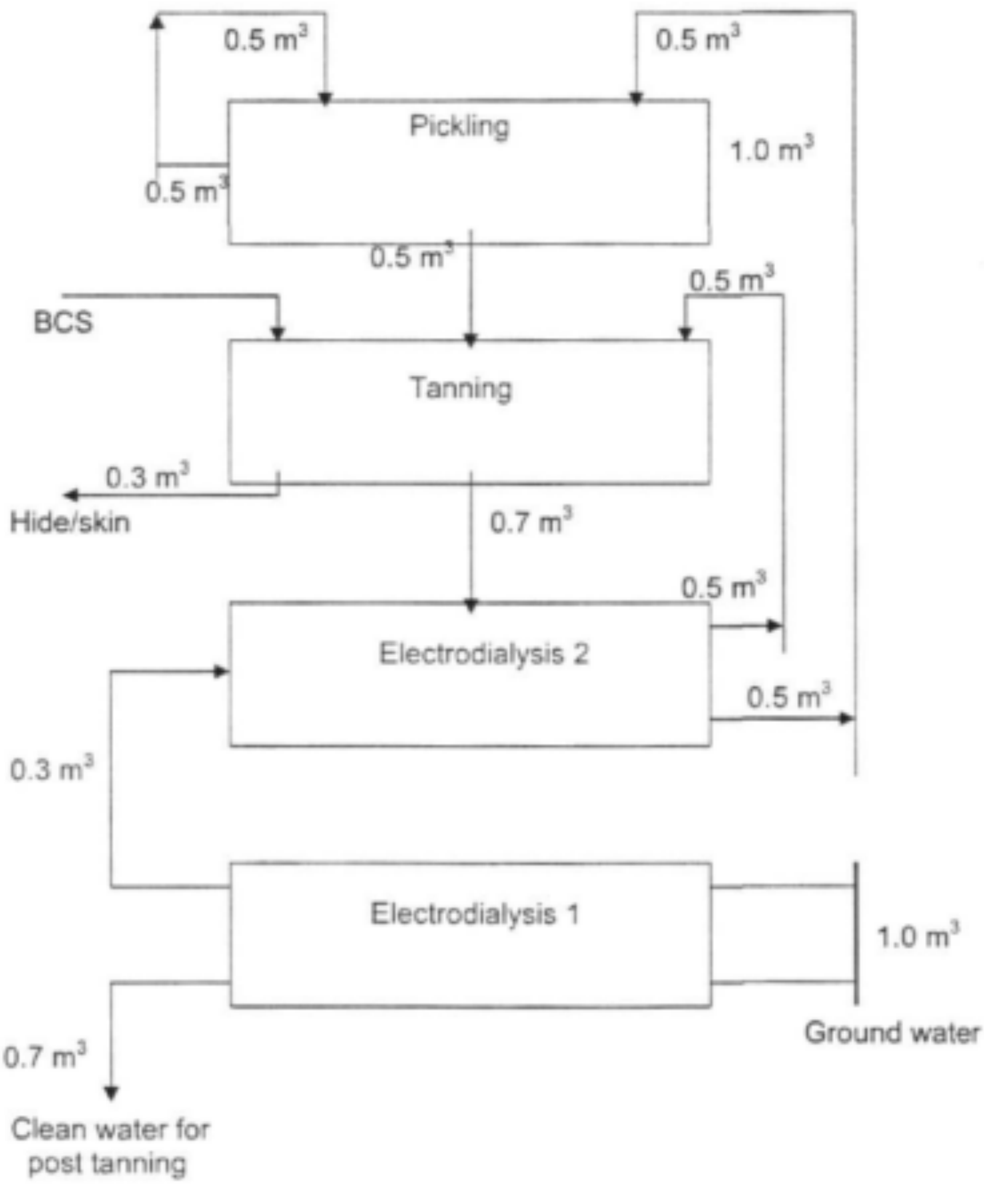


Figure 5: Schematic Representation of tanning process

7. NEW BRINE TREATMENT PLANT RECLAIMS PURE SALT AND PURIFIES WASTEWATER

7.1 INTRODUCTION

Gilet (1989) has described a brine treatment plant that reclaims salt and purifies water. In order to prevent an infectation of rawhides with putridactive bacteria and a breeding of the bacteria on the rawhides, the rawhides are usually preserved with the aid of common salt. The waste management of the salt quantities obtained thereby is disadvantageous in that the common salt, which is becoming increasingly expensive, can not be reused. Therefore, the price of the preserved hide is increased by 100% due to the expenses of purchasing common salt once again. Moreover, the conventional methods of "waste management" are hindered increasingly. Thus in the future, increased prices for conventional waste management must also be taken into consideration.

In the method described below, it is claimed that these difficulties can be prevented and the common salt can be reused. In this method both the desalting of the waste water and the processing of the waste salt are conducted in an economic manner. Moreover, official requirements which will be made in the future or already exist in some regions are taken into account. That means that no environmental pollution at all will occur by the plant described.

7.2 BRINE COLLECTION

The brine obtained in the preservation of raw-hides which consists essentially of proteins, calcium, sulphate, bicarbonate, sodium and chloride is collected in tanks designed to hold the required quantities (see 1.1 on Figure 6). It is no longer necessary to feed the brine into the sewage system. Thus, wastewater fees already existent and difficulties eventually arising with official authorities because of the salt proportion of sometimes up to 20%, are avoided. The wastewater fees may result from a withdrawal of oxygen in the waters caused by the introduction of such wastewaters. In the event that such measures are applied by the official authorities considerable expenses would arise – without a method such as the one described – in the field of waste management of the wastewater.

7.3 BRINE SEPARATION

The brine is supplied to the centrifuge (see 1.2) from the tanks described above. There the proteins contained in the brine, together with the said bicarbonates, sulphates and trace elements are separated from the remaining components, skimmed off and fed to a separate tank in the form of sludge.

The separation occurs with the aid of rotation using the different specific gravities of the individual substances. The remainder which is called "concentrate" in the following

description, consists essentially of common salt and water. At this stage an essential step directed to the further economic treatment and recovering of reusable substance is taken.
At this stage of the process the concentrate is fed to a vacuum tank (see 1.3). Steam is formed by controlling the temperature, and, caused by course of the operation, the common salt is substantially removed from the concentrate. This is removed from the vacuum chamber, and the steam still containing a proportion of about three-to-five percent salt is fed to a condenser via a separate drawing-off line. The waste heat created thereby is used, in turn, in the preheating of the concentrate. Because of the pressure conditions produced in the method, in turn, an optimum saving of energy is achieved.

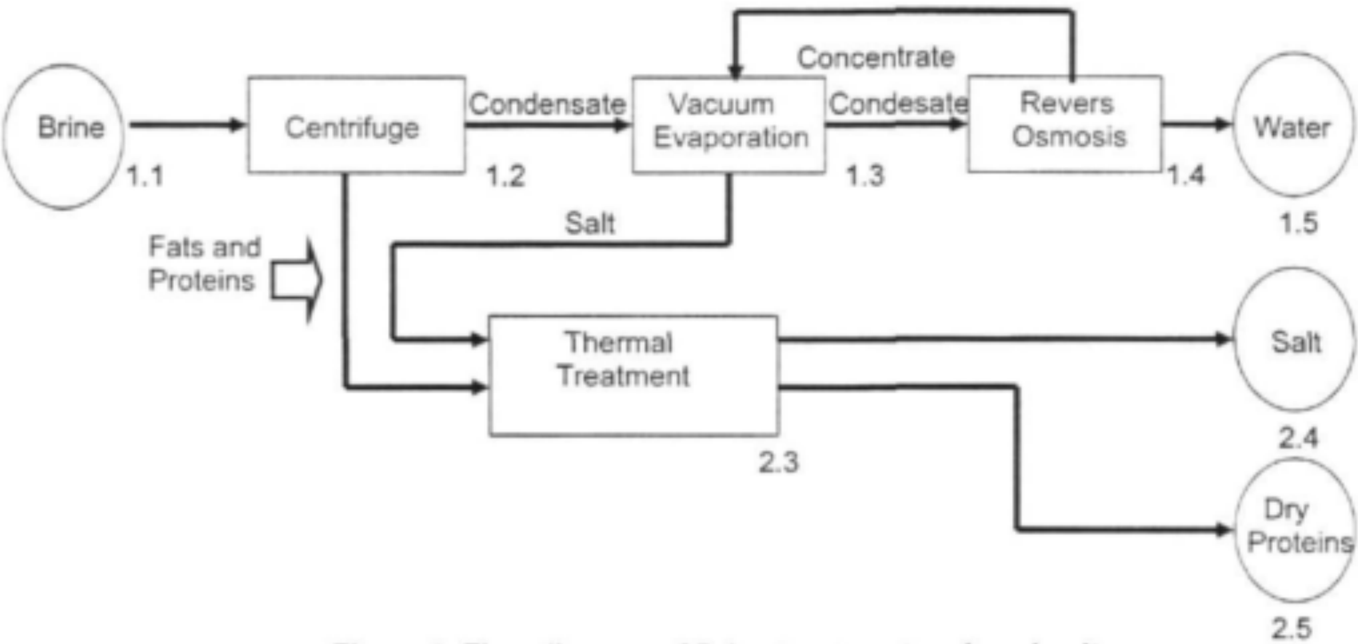


Figure 6. Flow diagram of Brine treatment and worksalt

At this stage the condensed steam is subjected to a further treatment in order to remove the three-to-five percent salt contained therein (see 1.4). A water is obtained as final product which is absolutely salt-free, just as drinking water is reclaimed from sea water, and is reusable from every point of view (see 1.5).

7.4 TREATMENT OF THE WASTE SALT

The waste salt obtained in the course of the operation is introduced into the preliminary tank without any addition of water. Similarly, the salt recovered from the vacuum evaporation (see 1.3) is fed to the preliminary tank automatically and mixed with the waste salt. In this respect, the tank size is designed in accordance with the quantity obtained each day in the plant (depending on the respective factory).

With the aid of mechanical devices it is ensured that foreign bodies present in the waste salt (i.e. glass, etc.) are separated from the waste salt, since it could eventually result in breakdowns during the thermal treatment. The charging from the supply tank likewise occurs mechanically and is fully automatically.

Because of the treatment temperature in the thermal treatment (see 2.3) predetermined in the method, it can be ensured that:

(1) The organic components are combusted completely.
(2) The recycled salt does not contain any microorganisms.

By these essential items it is guaranteed that no damages of the skin occur in the reuse of the salt. A continuous operation is provided in which a removal at any time is possible. On completion of the thermal treatment, it is ensured that any salt grain size desired by the respective customer can be obtained.

The waste heat produced is used simultaneously for the preheating of the concentrate and for the drying of the proteins which are present as a sludge from the centrifuge. At the same time, because of the closed system in the method, waste gases do not penetrate to the outside and are not released into the atmosphere unused. This ensures an economically optimal operation in accordance with the requirements with respect to the emission from every point of view. The obtained recycled salt is odourless and of perfect colour (i.e., white) and therefore fully reusable (see 2.4). The proteins obtained (see 2.5) can be delivered to feed and fertilizer traders. Because of the price obtained, treatment costs are covered, and even surpassed. A use of the sludge in wet form by local dead animal disposal agencies cannot be ensured in all places, as the dead animal disposal agencies mostly prefer the sludge obtained from slaughter-houses. In this respect the proceeds of this type of wet sludges may be questionable.

7.5 COST ANALYSIS

The consumption figures (see Table 12) are based on the experience that each raw-hide loses one US gallon of wetness at the race-way. Within that wetness there is a 20% salt content.

The treatment therefore is reduced on the surplus of liquid from the raw-hides at the race-way. Of course, if wished, the complete content of a race-way can be treated in a permanent way.

On an average 100 square meters of interior space are needed for one plant. Per day one man must spend about 30 minutes on the system. This manpower will be trained by the producer and therefore can be taken from the original staff of the plant. Maintenance by the producer takes place every six months, which takes 2 days.

In the construction of the plant described, it was taken into consideration at any time that the plant is operating in extreme environments (high salt pollution). These conditions were taken into account in the selection of the materials. Thus, all parts contacting salt or liquid media containing salt consist of the material no. 1.4571. Likewise, the durability in connection with the effect of salt was taken into consideration in the selection of the aggregates. For the reasons mentioned above the life of the plant can be placed at 5 years with proper maintenance. After this time a further life of 5 years can be achieved by an overhaul.

Table 12: An outline of expenses incurred by the system

Type of consumption	Consumption per raw-hide for:	
	treatment of brine	treatment of salt
Heat production Liquid gas	3,461 cu.ft	0.69 cu.ft
Power For drive and aggregate		0.01 kw/h
for pumps and aggregate	0,05 kw/h	

8. EVALUATION OF MEMBRANE TECHNOLOGY FOR THE TREATMENT OF IINDUSTRIAL EFFLUENTS

8.1 INTRODUCTION

Evaluation of membrane technology for the treatment of tannery effluents was described by Schoeman and Steyn (1992).

The salinity levels of tannery effluents discharged into the municipal water treatment system in South Africa 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 material 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 necessary 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 -1Xss pe rformance 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.

8.2 CONCLUSIONS

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 $\ell/m^2/d$. 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 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 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 30 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 analyzed.

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 mg/ℓ 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 concentrations 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.

Excellent conductivity removals were obtained during treatment of the effluent with cellulose acetate membranes. Conductivity removals varied between 79 and 88%. Feedwater conductivity to the RO unit varied between 2 580 and 4 290 mS/m. Permeate conductivity varied between 300 and 753 mS/m. Therefore, it should be possible to produce a water of suitable quality for discharge to the sewerage system.

It is estimated that the capital cost to treat 1 000 m^3/d of the final effluent produced by a tannery with tubular UF and RO membranes will amount to R12 million Rand (R5,4 million for tubular UF and R6,6 million for tubular RO; R4,0 million for spiral RO). Operating cost will amount to R5,65/m^3 for the tubular systems (R2,19/m^3 for UF and R4,0/m^3 for RO). Capacities, recoveries and the cost breakdown are shown in Appendix 3.

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 $A1^{3+}$ 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.

9. EVALUATION OF ULTRAFILTRATION AND MICROFILTRATION FOR SALT AND CHROMIUM RECOVERY FROM SPENT TANNING/PICKING EFFLUENT FOR REUSE IN THE TANNING/PICKLING PROCESS

9.1 INTRODUCTION

Ultrafiltration and microfiltration were described in South Africa for salt and chromium recovery from spent prickling/tanning effluent (Schoeman and Steyn, 1998).

Both UF and MF should be suitable technologies for salt and chromium recovery from spent tanning/pickling effluent. No information, however, is available on the fouling potential of the effluent for the membranes, and ways and means of cleaning fouled membranes. There is also no information available regarding process efficiency for salt/chromium recovery and organics removal from spent the tanning/pickling effluent with UF or MF technology.

The objectives of this investigation were, therefore, to evaluate UF/MF for salt and chromium recovery from the spent/pickling effluent, and to determine the preliminary economics of the process.

9.2 CONCLUSIONS

The sodium (22 600 mg/ℓ) and chloride (28 930 mg/ℓ) concentrations of the spent tanning/pickling effluent are high. The sodium chloride, however, is contaminated with organics (COD 9 880 mg/ℓ), chromium (3 900 mg/ℓ), iron (12,9 mg/ℓ), manganese (20,1 mg/ℓ), ammonia-nitrogen (2 019 mg/ℓ), and magnesium (2 560 mg/ℓ). The organics and metals should be separated from the salt before the salt can be considered for reuse in the tanning/pickling process.

Membrane fouling was experienced during the treatment of the spent tanning/pickling effluent with UF using polysulphone membranes. Initial tests on a laboratory scale UF module showed that it would be difficult to control membrane fouling with chemical cleaning. However, sludge conditioning with a polyelectrolyte prior to UF treatment showed that it should be possible to control membrane fouling easier with chemical cleaning than without sludge conditioning. Initial tests had also shown that approximately 62% of the organics in the effluent expressed as COD could be removed with UF treatment.

Membrane fouling was experienced during treatment of the spent tanning/picking effluent in a pilot scale UF unit using polysulphone membranes. Cleaning of the membranes with different membrane cleaning agents showed that it would be difficult to control membrane fouling. However, membrane cleaning results at elevated temperature, using Ultrasil cleaning agent, showed that it should be possible to control membrane fouling.

Excellent chromium (99,9%), iron (93,7%) and manganese (96,7%) removals could be obtained during neutralization of the effluent with magnesium oxide. Bacteria could be significantly removed (>96%) from the effluent with UF treatment.

COD removals with UF (polysulphone membranes) from the unneutralised feed varied from 27,7 to 50,91% in a number of cases. It further appeared that most of the organics were removed during the neutralization step. Organics removed from the unneutralised feed were 44,51% in once case, while only 16,2% organics could be removed from the neutralized feed with UF.

Carbosep UF membranes (metallic oxide membranes) with a molecular mass cut-off of approximately 10 000 Dalton showed that very little organics (expressed as COD) could be removed with the membranes (only 10,06%). Therefore, most of the organics in the effluent have a low molecular mass <10 000 Dalton. Bacteria removal of approximately 80% could be obtained with the membranes.

The dry solids in the neutralized sludge could be concentrated from 4 to 4,7 times in the UF treated sludge. The organic concentrations, however, of the UF concentrated sludge is high (16 to 20%). The chromium concentration in the UF concentrated sludge is high (8 to 10%), while the iron and manganese concentrations are low (approximately 0,08%). The magnesium concentration, however, in the sludge is high (6 to 7%). The suitability of recovering chrome for reuse in the process should now be investigated.

Permeate flux decline was also obtained during the MF treatment of the effluent. This flux decline can be ascribed to the compaction of the sludge solids on the polyester membrane surface. The decline in the permeate flux could also be ascribed to membrane fouling. Membrane fouling, however, should be easily controlled with MF of the effluent because the membrane could be renewed with each treatment cycle.

The MF tests results also showed that most of the organics in the effluent (expressed as COD) were removed during the neutralization step. Approximately 44 to 54,1% of the organics were removed in one case, and from 59 to 69% in another case. Only 7 to 11% of the organics were removed in the MF step.

Very good chromium, iron and manganese removals were also obtained during the MF treatment of the effluent. Bacteria and oil removals of 99,9 and 91,2% were obtained, respectively.

The dry solids in the MF feed could be concentrated from 3 to 5 times in the concentrated MF brine. The organics and chrome concentrations in the sludge were high as before, while the iron and manganese concentrations were low. The magnesium concentration of the sludge was also high.

It was demonstrated that nanofiltration treatment of the MF permeate could remove approximately 55% of the organics from the MF permeate. Therefore, a much better removal of organics could be obtained with nanofiltration treatment. Approximately 70% of the sodium and chloride in the MF permeate could be recovered with nanofiltration. Approximately 94% of the bacteria in the MF permeate could also be removed with nanofiltration treatment. Fouling of the nanofiltration membranes by organics in the feed may be a problem. However, initial results have shown that it should be possible to control membrane fouling with chemical cleaning.

10. REDUCE POLLUTION LOAD AND IMPROVE PROFITABILITY

10.1 INTRODUCTION

The use of cleaner technology options in the tannery industry has been described by Sahasranaman and Emmanuel (1997).

Tannery pollution control of late has become a serious matter in India. While efficient treatment of effluent at the end of pipe is widely attempted, in-house measures to eliminate/reduce pollution load in effluents has not yet received due attention. The old adage, "prevention is better than cure" is as much relevant to industrial pollution as to human health. The regional program of UNIDO, through its India project US/IND/90/244 promoted some cleaner technologies in the tannery sector. Such technologies (e.g. chrome recovery, enzymatic unhairing) are finding increasing acceptance in the industry."

In this section, cleaner technologies appropriate for a small/medium scale tannery are briefly presented. The verified results of cleaner technology measures adopted by a small scale tannery in Vaniyambadi have been presented to prove that cleaner tanning is eminently viable technically and commercially in a small/medium scale tannery. What is needed is commitment to the cause.

10.2 CLEANER TECHNOLOGY OPTIONS

The various cleaner technology measures being tried currently includes the following (see Table 13).

Many experiments are currently undergoing in the state of Tamil Nadu. Some enterprising small and medium tanners have taken such practices on their own, achieving considerable success. A brief report on the present situation with regard to the experiment is attempted below:

Table 13: Cleaner Technology Options

The various cleaner technology measures being tried currently includes the following:

Sl No.	Cleaner Technology Options	Impact on Pollution Load
1	Salt free hide & skin preservation	Helps eliminate salt & reduce TDS
2	Mechanical desalting	- do -
3	Counter current soaking	Reduced water consumption
4	Enzyme assisted soaking	Reduced water consumption & processing time
5	Green fleshing	Reduced chemical consumption & quantity of solid waste
6	Enzymatic sulphide-free unhairing	Reduced concentration of sulphides, COD, etc. in effluent
7	Lime splitting	Reduced chemical consumption & solid waste
8	Hair saving unhairing-liming	Reduced concentration of nitrogen, BOD, COD etc. in effluent
9	Direct recycling of liming floats	Reduced chemical & water consumption & reduced BOD, COD & sulphides in effluent
10	Automatic water/chemical	Reduced water consumption dosing systems
11	Ammonia-free deliming using alternate deliming agents such as carbon dioxide gas	
12	Chrome recovery, high chrome exhaustion and/or chrome liquor recycle	Reduced concentration of chromium in effluent
13	Through-feed dyeing with spent dye liquor recycle	Reduced colour BOD, COD, etc. in effluent
14	Reduction in water consumption by better housekeeping methods	Reduced water consumption

(a) **Alternate raw hide and skin preservation methods**

Control of TDS, though not regarded as serious in many other countries, is vital for Tamil Nadu due to degradation of ground water in many parts of the state. The feasibility of the salt free preservation, however, unviable it may seem, should be examined and tried. UNIDO is considering the option of utilization of solar drying of raw hides and skins as a means of preservation. Presently there has hardly been any work in this direction.

(b) **Mechanical desalting**

A mechanical desalting process has been demonstrated by UNIDO in one or two tanneries and now some more tanneries have shown interest for the installation of mechanical desalting drums. The process has been found to be simple and successful in removing between 15% and 30% of the salt content from the hides. The solid salt separated out could be cleaned and used in pickling and thereby enabling cost saving.

(c) Enzyme assisted soaking has been tried by a number of tanneries and it has been noted that by adopting this process, the soaking time can be reduced up to 40%.

(d) Many tanneries in Ranipet and Vaniyambadi have already adopted a counter current soaking process, i.e., utilizing spent soak liquor from the second wash for the dirt soaking. This method has helped in reducing the water consumption in the section by 50%.

(e) Green fleshing, i.e. fleshing of raw hide after soaking, is being done by only very few tanneries. Those who have adopted this process are happy with the results. There are, of course, practical difficulties in a wider adoption of this practice.

(f) Enzymatic unhairing: Many tanneries processing both hides and skins have tried enzymatic unhairing and some tanneries are regularly using enzymes for reduced the sulphide application in the unhairing process. Many suppliers of enzymes, both domestic and foreign have come into the market since UNIDO/CLRI started the experiment in two tanneries in Pallavaram and Vaniyambadi. Spic and Textan are two Indian companies dealing with enzymes, and many foreign companies like JOB, UK, Buckman Laboratories USA and Nova Nordisk, Denmark have begun supplying these enzymes. It has been noted that enzymes can achieve even 100% replacement of sulphides in processing of goat/sheepskin and up to 70% reduction of sulphides in case of hides. Generally, however, it has been observed that enzymes help considerably to reduce the application of sulphides but not its total elimination.

An observation done by UNIDO in a tannery processing buffalo calf skins in Ranipet in an experiment with enzymes revealed the following points : -

- Utilization of 0,15% of enzyme was enough to reduce the sulphide utilization from 3% to 1,5% in the unhairing process. (The enzyme tried was from Nova Nordisk, Denmark).

- The degree of unhairing was found to be the same as that of normal sulphide unhairing.

- The resultant after deliming was found to be cleaner, with less wrinkles, compared to normally processed hides indicating a better area yield.

- The reduction of sulphides in the effluent from the unhairing section was noted to be as high as 72% in this case compared to normal unhairing. The reduction of COD in the effluent stream was found to be 25%.

- The cost of operation in terms of cost of chemicals alone was found in the conventional and the enzyme assisted process.

In cases of sheep and goat skins, many tanneries are regularly utilizing enzymatic unhairing to completely replace the sulphides.

(a) Hair saving unhairing liming process using HS drums has been quite effective in European tanneries. This process is capable of reducing 15 – 20% COD and 25 – 30% of total nitrogen in the effluent. RePO, UNIDO is planning installation of the HS process system in one of the tanneries in Ambur in the first half of 1997.

(b) Direct recycling of liming floats has been attempted by some tanneries. Conclusive data over a period of time is yet to be obtained.

(c) Automatic water/chemical dosing systems have been installed by some tanneries. Though comparison over a period of time has not been done so far, it is expected that such automation may result in 15 – 20% savings in water and 10 – 15% savings in chemical consumption, besides a more consistent quality product.

(d) Carbon dioxide deliming: Deliming with carbon dioxide, instead of ammonium salts, reduces the nitrogen content in the effluent by 40% and results in better quality pelts. UNIDO has successfully demonstrated this application technically. Experience indicates that CO_2 deliming is more successful in skins than in hides.

(e) Chrome recovery, the most successful cleaner technology demonstrated so far, is being discussed in detail elsewhere and, therefore, not discussed in detail here. Moreover, CLRI has been demonstrating the chromium management systems such as direct recycling of spent chrome and high chrome exhaustion in tanneries in different parts of the country.

(f) Through-feed dyeing process, which enables one to recycle exhausted dye baths continuously without discharge in the effluent, apparently has not been attempted so far in India. These machines are becoming more and more popular in Europe.

10.3 RESULTS OF VARIOUS MEASURES ADOPTED BY THE TANNERY

The various measures adopted by the tannery have produced a notable reduction in water consumption and pollution load in the effluent. RePO Madras of UNIDO studied these aspects and the salient details are shown in Table 14 and 15: -

Table 14: **Effluent Streams Recycle**

Process Modification	Observed Reduction in Water Consumption	Observed Reduction in Total Pollution Load (in terms of BOD)
Counter current soaking process	30%	—
Reuse of reliming liquor in liming process	3%	4%
Reuse of liming liquor in soaking	3%	39%
Use of soak liquor prior to fleshing in washing fleshing machine	5%	—
Recovery and reuse of spillage from pasting section in sulphides	1%	20%
Better housekeeping	3%	3%
Total	**45%**	**46%**

Table 15: Cleaner Technologies and Others

CLEANER TECHNOLOGIES AND OTHERS			
Process Modification	**Unit Constructed**	**Observed Reduction in Total Water Consumption**	**Obserbed Reduction in Total Pollution Load**
Chrome recovery system	Full Chrome	—	90% of the chromium
Enzymatic unhairing	None; change in operation		100% sulphide (if regularly operated)
Installation of two no solar panel heating system for water heating (6 more panels under procurement)	Solar panels, heaters, pipelines		Reduced fuel consumption in tannery by 30%

10.4 Cost Benefit Analysis of these Measures

Effluent recycles: It has been noticed that the recovery and reuse of effluent streams have resulted in an overall reduction of 45% each in water consumption and pollution load. The overall cost of these installations was Rs. 56 000. Assuming that water bought by the tanneries cost Rs. 20 per 1 000 liters, a national saving of Rs. 300 per day may be estimated as saving in this regard.

The financial implications of cleaner technology measures are shown in Table 16.

Table 16: **Financial Implications of Cleaner Technology Measures Adopted / Proposed by the Company**

Process Modification	Unit Constructed	Expenditure (Rupees)
Reuse of reliming liquor in liming process	Collection tank, pump, pipelines	20 000.00
Counter current soaking process	None (only operational practice modification)	—
Reuse of liming liquor in soaking	Collection tank 2 Nos., pumps, filter, sludge filter	30 000.00
Use of soak liquor prior to fleshing in washing fleshing machine	Collection tank (1.0 m x 1.5 m x 1.5 m)	5 000.00
Recovery & reuse of spillage from pasting section	Collection tank (300 liter capacity)	1 000.00

10.5 IMPROVEMENTS DONE IN A SMALL SCALE TANNERY IN VANIYAMBADI

The verification of the results are as follows : -

M/s. Mohammed Usman & Co. is a small scale tannery in Vaniyambadi, processing approximately 2 000 kg (100 pieces) of sheepskins per day. The tannery has introduced a number of water conservation and cleaner technology measures as part of a waste minimization program promoted by the National Productivity Council and UNDP assisted NLDP. Some details of the measures adopted by the tannery and the results obtained are discussed briefly here.

Important modifications done by the tannery include : -

(a) Recycling of effluent streams

- Counter current soaking: The spent soaking liquor from second washing is being used in the first soaking. The arrangement didn't require any new construction, but only a change in operation practice.

- Collection and reuse of spillage during the bating unhairing bath: The arrangement consists of a small collection tank to collect the spillage of lime sodium sulphide paste and the collected slurry is used in the next batch of pasting.

- Utilization of spent reliming liquor for liming: The reliming process in the tannery is being done in paddles. The spent liquor amounting to 3.3 m^3 is collected in an underground tank with an effective volume of 3.3 m^3 and the volume is pumped to the liming pits for the liming operation.

- Utilization of spent liming liquor amounting to 3.3 m^3 is first collected in a settling tank. After settling for 3 – 4 hours, the supernatant is pumped to a sand filter and the filtrate is collected in another collection tank. There the spent liming liquor is diluted five times with fresh water and make up to the required volume for soaking and is then pumped to the soaking pits. The sludge that settles in the bottom of the tanks is pumped to a sludge drying bed.

- Utilization of spent washing prior and after the fleshing process for washing the fleshing machine: The wash/rinse water used to wash the skins before and after the fleshing operation is discharged into a collection tank with a capacity of 2.25 m^3 and from there the water is pumped for washing the fleshing machine during the fleshing operation.

(b) Cleaner technology measures

- Chrome recovery unit : The tannery has installed a chrome recovery unit of 4 000 liters/shift capacity. The recovered chrome is found to be good in quality. Total installation cost of the chrome recovery unit inclusive of all civil and electromechanical components is around Rs. 450 000.

- Installation of a solar powered heating system : The tannery has installed two solar panel powered heating systems to supply hot water to the dyeing section.

- Enzymatic unhairing : The tannery has tried enzymatic unhairing with various enzyme samples available in the market. The enzyme supplied by SPIC has been observed to be producing good results in the tannery with a total replacement of sulphides. However, the cost of operation was observed to be higher than the conventional lime-sulphide process and the experiment with enzymes is still going on.

- Other cleaner technology measures, like mechanical desalting and carbon dioxide deliming, are in various stages of implementation in the tannery.

Apart from the above, the tannery has adopted several measures as part of their modernization process. However, have a strong bearing on the reduction of the pollution load. The measures include : -

- Conversion of paddle deliming into drum deliming.
- Installation of a computer network for constant monitoring of material input in the various sections of processing.
- Installation of a full fledged chemical laboratory.
- Installation of a computerized flow measurement system.

- Installation of an automatic water dosing system.

The effect of these investments is particularly relevant when the installation of an individual effluent treatment plant is considered. For a total volume of 35 m^3 per day (other than the soak liquor), an effluent treatment plant would cost around Rs. 800 000 rupees and now for an effluent volume of approximately 20 m^3 per day(as the water saving achieved is 15 m^3 per day), approximately Rs. 550 000 may be required. This is a saving of 2.5 lakhs, besides recouping investments on the arrangements required for the recycle of the effluent treatment plant. Besides an average savings of approximately Rs. 10 000 per month on the cost of operation of the effluent treatment plant may be possible.

One question may be raised here – if the effluent treatment plant is already constructed, what benefit other than the savings in operational cost can be achieved? Well, if there is already an operational effluent treatment plant, the simultaneous reduction will enable one to process double the quantity of effluent, which allows you to process double the production capacity, provided other conditions like raw material availability, space in tannery, etc. are favourable. The profit from possible additional production could be interesting to the enterprise.

(c) Other cleaner technologies

The chrome recovery unit has been observed to be producing a financial savings of Rs. 2 720 per batch (two batches in a week), thus giving a savings of Rs. 21 760.00 per month. The pay back period thus calculated would be 18 months.

10.6 CONCLUSION

The results of the experiments made in this small tannery is quite impressive. Other tanneries should also come to adopt similar simple techniques to produce such good results in conservation of a valuable resource, namely water, and to reduce the pollution load at the same time generating considerable benefit out of these modifications. Any tannery interested to getting more information on these measures are welcome to contact: RePo, UNIDO, TNPCB Building, 100, Anna Salai, Guindy, Chennai – 600 0932.

11. DISCUSSIONS WITH SA LEATHER EXPERTS AND OTHER EXPERTS

Discussions were held with South African and overseas leather experts to try to establish the application acceptability and economic feasibility of using membrane technology in the leather industry. The following emerged from the discussions : -

Guiseppe Clonfere (g. Clonfero@liberto.it) (Italy), has discussed the salt treatment topic with the director of (UOI-ODEPUR), a big common effluent treatment plant for tannery effluents located in the leather district of Santa Crocesull' Arno (Pisa). This person is well informed about the situation in 3 Italian leather districts and any new technical development. These are the results of this investigation : -

(a) At the present there are no plants (neither on pilot nor on industrial scale) treating salinity of tannery effluents.

(b) Mechanically shaking the hides and skins before processing is the only system adopted by the Italian tanneries for somewhat reducing the chloride content in the effluent.

(c) Salinity, of course, remains a big problem, but if somebody is investigating possible treatment methods, this is done without publicity.

(d) At present, solar evaporation is the only system for eliminating salts adopted in some hot climate countries (of course not in Italy).

Warren Bowden (warren@blcleathertech.com) from BCL (UK), said that to his knowledge there are only a handful of membrane plants in application within the tanning sector, primarily in Italy and primarily of ultrafiltration of process liquors for chemical recovery. To the best of his knowledge, nanofiltration and RO have not yet been applied (although they are working on it). The economics of the process cannot be provided for a number of reasons :

The cost of water (discharged or purchased), varies not only per country, but also per site, which means that to justify the recovery or reuse of water following such intensive treatment requires case by case analysis. There may be other "political" reasons for persuing such technology. On occasion, a compliance issue may require application of such technology – so economics become less relevant. He is aware that RO costs are now falling dramatically, and that this technology has begun to be taken up by the textile sector. Some BLC members are also at advanced stages of consideration of this technology with BLC. However, it is worth remembering that BLC's role is to develop technologies for the leather sector by overcoming technical barriers and not to sell the technologies per se.

Guiseppe Clonfero (g. Clonfero@liberto.it) (Italy), said that he has no information about plants in operation in Europe for the treatment of dissolved salts of tannery effluents on industrial or pilot scale. Nevertheless, he knows that the topic is very interesting and there are private groups studying it and making trials. Their aim is to commercialise systems and therefore they do not give any information away.

Peter Howard from Pelts Products (Port Elizabeth) says that it is essential for Pelts to use membrane technology to solve their salt problem. It has to happen. Johan Barnard from EnviroTon says that effluent discharge standards must be enforced by the authorities. This will ensure that membrane technology will be used in the leather industry. The cost of the technology should also be affordable.

Peter Howard further says that they must in future be in the position to solve their salt problem. Therefore, they must position themselves. Chromium and salt should be recovered for reuse. Effluent discharge standards will become tougher in future. Therefore, technology must be applied or plants can be closed. Overseas people may not buy our leather for motor seats manufacture unless we are not removing pollution from tannery plants.

Peter Howard also says that the pollution from salt discharges in the tannery industry is a big issue. There are at least 3 big tanneries with salt problems in the Port Elizabeth area.

Pelts is allowed to discharge 10 000 mg/ℓ chloride to sewer or 3 tons salt per day. Pelts, however, do not always comply with the requirement. Pelts would like to treat, soak and pickling effluent for salt reduction. Chromium is recovered. Pelts discharge 1 300 m^3/d of effluent to sewer.

Nico Sneider from Seton (Nigel) says that membrane technology will be acceptable to the tannery industry when it works well and is cost-effective. Operational cost should not be more than current running costs. The current running cost at Seton for example is approximately R5 000 000 per annum.

Nico Sneider thinks that membrane technology is currently not an economically feasible technology for use in the leather industry. The big issues facing them are salt and sulphate discharges. Chromium is recovered at Seton. Seton is allowed to discharge 500 mS/m conductivity. Currently they discharge 650 mS/m. Therefore, they are exceeding the limits. Sodium and chloride discharges of 1 000 and 500 mg/ℓ are allowed, respectively. They are almost there. Seton would also like to reduce sulphides in their effluents.

Seton is not using salted hydes anymore. However, they still use salt for pickling and this is a problem. Salt is also used in the dyeing process.

Seton is considering it to pipe their effluent to Erwat for further processing at the Sewage Works. Seton can also separate streams in their plant which will make treatment with membrane technology easier. The disposal of brine from a desalination plant will be a problem.

Athol Pratt of Bader Bob says that they are currently only doing finishing. There are no wet blue activity anymore. Effluent from washing and dyeing is discharged to sewer.

The effluent discharge standards should become stricter according to Athol Pratt. Technologies for effluent treatment will then be implemented. The bottom line is that effluent should be treated according to legislation or the factory should be closed. Technology should have a track record before being implemented in South Africa according to Athol Pratt.

12. LIST OF TANNERIES

A list of Tanneries in South Africa is shown in Table 17.

Table 17: List of Tanneries in South Africa

Tannery	Contact	Address	Tel. No.	Fax No.
African Hide Trading Corporation	Mr Hennie Roets	P O Box 1067 Port Elizabeth 6000	041-4057000	041-4612114
Bader Bop Brits Leathers	Mr Eddie Naude Jan de Klerk	P O Box 911-875 Rosslyn 0200	012-7977100	012-7977150
Butterworth Tannery		P O Box 135 Butterworth 4960	047-4920256	047-4920269
EAC Tannery	Mrs Therina Terblanche	P O Box 63323 Vaalpark 9573	016-9721802	016-9722282
Eagle Ottawa SA	Mr Chris O'Neill	P O Box 2332 Bronkhorstspruit 1020	013-9333417	013-9333507
Era Pelle's Tannery	Ms Belinda Kruger	P O Box 22 Burgersdorp 9744	051-6531273	051-6531273
Fisgriver Tanning Co.	Mr Justin du Plooy	P O Box 1407 Rant en Dal 1751	011-6602929	011-6608781
Gauteng Leather Works	Mr Alwyn van Deventer	P O Box 304 Middelburg 5900	049-8423690	049-8422603
Gauteng Ostrich Tannery	Mr Andre Strauss	P O Box 3686 Randgate 1763	011-4162260	011-4162020
Gringo Leather	Mr Pierre van Niekerk	P O Box 54160 Marburg 4252	039-6855345	039-6855343
Hannitan Leathers	Mr Rudof Hanni	P O Box 3820 Springs 1560	011-8172150	011-8175259
Hidskin Processors	Mr Charles Austin	P O Box 86350 City Deep 2049	011-6136271	011-6136708
Horne Tanning	Mr Mike Horne	P O Box 2211 Grahamstown 6140	046-6228174	—
Iole Tanning Services	Mr P Castopolie	P O Box 2800 Vereeniging 1930	016-4554301	016-4553026
Klein Karoo Co-op	Mr Allan Wallace	P O Box 241 Oudtshoorn 6620	044-2741483	044-2741588
Kolosus Automotive Leather	Mr Braam Keyser	P O Box 825 Ladysmith 3370	036-6383000	036-6383033
Kwiktan	Mr John Lewis	P O Box 5307 Krugersdorp West 1742	011-6603926	011-6653633

Tannery	Contact	Address	Tel. No.	Fax No.
Leather from Hart (Sutherlands)	Mr Wynand Hart	Suite 188, Postnet X6, Cascades 3202	033-3985700	033-3981272
Mario Levi (SA)	Mr Tony Stottelaar	P O Box 3063 Uitenhage 6230	041-9921160	041-9921163
Mossop-Western Leathers	Mr Andre Pelser	P O Box 501 Wellington 7655	021-8649300	021-8641272
North West Tanning	Mr Jan du Plessis	P O Box 1766 Mogwase 0314	014-5583098	014-5582082
Oasis Tanning	Mr Andre van der Merwe	P O Box 5577 West Krugers-dorp 1742	011-4162270	011-4162265
Oscroc (African Game and Art)	Mr Andre Pienaar	P O Box 179 Florida 1710	011-9534932	011-9534932
Ostriches Galore	Mr Coen Grobler	P O Box 3983 Rustenburg 0300	011-4161061	011-4161208
Ostriland Import Export	Mr James McGill	P O Box 345 Citrusdal 7340	022-9212177	022-9212157
Outeniqua Tanning	Mr Robbie Peschel	P O Box 2068 George 6530	044-8781320	044-8781348
Ostrimark Tannery	Mr Johan Schoeman	P O Box 7074 Grahamstown 6141	046-6035300	046-6035301
Pelts Products	Mr Peter Howard	P O Box 323 Port Elizabeth 6000	041-4611515	041-4611203
Philippe Genuine Ostrich Products	Mr Phillip Vermaak	P O Box 52 Grahamstown 6140	046-6226567	
Prince Albert Tannery	Mr Peter Schneekluth	P O Box 103 Prince Albert 6930	023-5411411	023-5411255
Rein Tanning	Mr Kevin Hopewell	P O Box 10409 Dana Bay 6510	044-6977031	044-6977895
Richard Kane	Mr Richard Silber	P O Box 222 Maitland 7404	021-5351122	021-5114718
Seton SA	Mr Richard Delfel	P O Box 537 Nigel 1490	011-3607500	011-8146402
Southern Cape Ostrich Tannery (Scot)	Mr Pieter Yzelle	P O Box 2620 Mossel Bay 6500	044-6977100	044-6977105
Swartland Tannery	Mr Paul Jooste	P O Box 849 Wellington 7655	021-8731061	021-8732895
Tanrite	Mr Jacques Barkhuizen	P O Box 920 Uitenhage 6230	041-9924887	—

Tannery	Contact	Address	Tel. No.	Fax No.
The Ing Thing	Mr Mike Ing	P O Box 254 Hilton 3245	033-3431445	033-3431445
Woods Tannery	Mr Andy Wood	P O Box 1603 Uitenhage 6230	041-9922179	041-9922144
Springbok Trading (EHSTCape Tanning)	Phillip Staples	Uitenhage	041-4612352	041-461855

13. GENERAL DISCUSSION

The main aim of this project was to conduct a techno-economic study to establish the viability of developing microfiltration/ultrafiltration/nanofiltration process technology for the recovery of chromium and salt from spent pickling/tanning effluent for reuse in the process. Pilot studies conducted overseas have shown that it should be viable to use a combination of microfiltration/ultrafiltration/nanofiltration for chromium and salt recovery from spent pickling/tanning effluent. However, no full-scale application of this technology has yet been implemented although it has been demonstrated that the technology should be technically and economically viable.

A lot of applied membrane research have been conducted in Italy, the UK and India to evaluate membrane technology for the treatment of tannery effluent. The only full-scale application that has arisen from these efforts is that of the use of ultrafiltration for the recovery of sulphide from the unhairing process. Interesting studies have also been conducted in India to evaluate reverse osmosis for the treatment of the final effluent produced by a tannery. The results look promising. However, it also appears that no full-scale application of reverse osmosis technology for the treatment of the final effluent produced by a tannery has yet been implemented.

It is clear from literature information that potential exists for membrane technology to be applied for the treatment of soaking (UF), liming (UF), deliming-bating (UF), degreasing (UF), dyeing (RO) and the final effluents (RO, membrane reactor) produced by tanneries. The soaking effluent has the highest saline concentrations of these effluents. Therefore, attempts should be made to recover salt from this effluent with UF for use in pickling to reduce the salinity of the final effluent produced by tanneries.

Tanning effluents have a very high fouling potential. Therefore, cleaning procedures should be developed to clean fouled membranes. This information and process design criteria for the treatment of tannery effluent are not available because companies involved in research keep the information to themselves for commercial reasons. Effluents also differ from each other with the result that general process design criteria are not available. Therefore, process design criteria for the treatment of tannery effluent should be developed if we would like to treat tannery effluent with membrane technology in South Africa.

The South African leather industry is of the opinion that it should be acceptable to use membrane technology for the treatment of tannery effluent. However, the industry will feel at ease with the technology once a track record has been established overseas.

The South African leather industry feel that it is not economically feasible to use membrane technology for the treatment of tannery effluent at present. Although it has been shown in this investigation that it is energetically economical. This attitude, however, might be based on insufficient information. However, this attitude should change if effluent discharge standards are enforced and if discharge requirements become stricter. This, of course, will happen in future with the result that membrane technology will be implemented for the treatment of tannery effluent. The time is now ready to invest in applied research to develop membrane technology for the treatment of spent tanning/pickling effluent, soaking effluent with its high salt concentration and for the final effluent produced by a tannery.

Cleaner technology options are available for the treatment of tannery effluent. These options include:

(a) salt free hide preservation;
(b) mechanical desalting;
(c) counter current soaking;
(d) ammonia-free liming using alternate deliming agents such as carbon dioxide;
(e) reduction in water consumption by better housekeeping;
(f) chrome recovery, high chrome exhaustion and/or chrome liquid recycle;
(g) etc.

Large savings can be obtained by implementing cleaner technologies at tanneries. Payback for chromium recovery are estimated at 18 months. Consequently, cleaner technologies should be implemented at tanneries as far as possible.

14. SUMMARY AND CONCLUSIONS

14.1 INTRODUCTION

The main aim of this study was to perform a techno-economic study to establish the viability of developing microfiltration/ultrafiltration/nanofiltration process technology for the recovery of chromium and salt from spent pickling/tanning effluent for reuse in the process. The secondary aim of the study was to determine the viability of developing ultrafiltration/reverse osmosis technology for the desalination of the final effluent produced by tanneries. The techno economic study was done to : -

(a) establish the international use of membranes in the application, and
(b) obtain an indication of the economical feasibility and acceptability of the use of membrane technology in the South African leather industry.

A considerable amount of applied laboratory and pilot research studies have been conducted overseas to evaluate membrane technology for the treatment of tannery effluent for product and water recovery and pollution control. Most of these studies are conducted in Italy, the UK and in India. However, it appears that the only full-scale application at present of membrane technology in the leather industry is the use of ultrafiltration for the recovery of sulphide from the unhairing process. Laboratory and pilot studies have demonstrated that potential exists for membrane technology to be applied for the treatment of tanning, pickling, soaking, liming, deliming-bating, degreasing, dyeing and the final effluent produced by tanneries.

The South African leather experts are of the opinion that membrane technology is an acceptable technology for the treatment of tannery effluent. However, they will feel more at ease with the technology once a track record has been established. The leather experts also feel that membrane technology is at present not an economically feasible technology for the treatment of tannery effluent. However the technology should become economically feasible with stricter effluent discharge requirements as well as with the requirements of the ISO 1400 standards.

14.2 CONCLUSIONS

14.2.1 Chromium tannage

It was demonstrated in pilot studies that a combination of ultrafiltration and nanofiltration should be effectively applied to recover chromium for reuse in the tanning process. The recovered chromium was used for tanning and the treated skins were compared with control skins treated with fresh chromium solutions. Analysis performed on the experimental skins revealed values very similar to those obtained on the control groups. Recovered salt from the nanofiltration process should be used for pickling.

14.2.2 Pickling

Reverse osmosis should be a suitable technology to treat the exhausted bath to recover salt for reuse in the pickling process. The RO permeate should be suitable for the preparation of soaking baths or as washing water. Pilot studies, however, will be required to develop process design criteria for this proposed application.

14.2.3 Final effluent

It was demonstrated in experimental studies that it should be possible to apply RO for the treatment of the final effluent produced by tanneries. The effluent, however, should be properly pretreated prior to RO desalination. The treated effluent should comply to the discharge quality requirements. Membrane fouling, however, will be a problem during RO treatment of the final effluent and fouling control will be an important aspect for the successful application of this technology. Pilot studies should be conducted to develop process design criteria for a full-scale application.

Organics in the final effluent should be reduced by a membrane bioreactor. The sludge should be concentrated sufficiently with UF membranes for the successful aerobic or anaerobic degradation of high molecular mass organics. The UF permeate containing less organics should be suitable for further desalination of the effluent. However, pilot studies will be required to develop process design criteria for a full-scale application.

14.2.4 Soaking

Ultrafiltration is proposed for the treatment of soaking effluents for salt recovery for use in the pickling process. However, this approach will need experimentation in order to obtain data to define its application.

14.2.5 Unhairing

Ultrafiltration is used on a commercial scale for the recovery and reuse of sulphide from the unhairing process. This appears to be the only full-scale application of membrane technology at present in the tanning industry. The use of an unhairing enzyme to reduce sulphide from about 10 to 1,5% is a new approach to reduce the sulphide which can also be recycled with UF. However, its use in the various tanneries will require preliminary pilot testing to adjust the working recipe for obtaining a specific product.

14.2.6 Deliming-bating

Ulftrafiltration is proposed to reduce fatty substances and COD from the exhausted bath of the deliming-bating process. The clear solution (permeate) can be reused for the preparation of new bating baths or as washing water after appropriate testing. Pilot studies will be required to develop criteria for the application of this process.

14.2.7 Degreasing

It was demonstrated that UF should be a suitable technology for the removal of fatty substances from degreasing baths. A reduction of the washing cycles normally employed to remove lipidic substances from the skins can be achieved as well as a reduction in water consumption. The payback period of an UF plant it estimated to range between 1 and 4 years. However, more data on the performance of a pilot plant are required for a more complete cost analysis.

14.2.8 Vegetable tannage

The UF process is proposed to recover vegetable tannins from the tannage process for reuse in the process. The permeate with a low organic concentration could be sent to a wastewater treatment plant.

14.2.9 Dyeing

The reverse osmosis process is proposed to recover dyeing substances for reuse in the dyeing process. The permeate solution could be reused as washing water or for the prepar ation of new dyeing baths. However pilot studies will be required for each case.

14.2.10 Direct and indirect energy savings

Membrane processes integrated with chrome and salt recovery (UF and NF), unhairing-liming (UF) and degreasing (UF) treatment are energetically economically. Therefore, it should be viable to develop these processes further for the treatment of tannery effluent.

14.2.11 Operation of a RO pilot plant *in India* for the treatment of the final effluent produced by a tannery

Membrane fouling problems were experienced during the operation of a RO pilot plant in India for the treatment of a final effluent produced by a tannery. This problem and operating experience will possibly lead to a full-scale application of RO for the treatment of tannery effluent in India. Treatment costs were determined at US $ 1,15 per cubic meter recovered water. Studies involving the utilization of the RO rejects have shown that it should be possible to recover salt after evaporation of the RO concentrate and use it in the pickling process. A watching brief should be kept in this development.

14.2.12 Colour removal from tannery dyeing wastewater with ultrafiltration

Ultrafiltration is a suitable process to decoulorise the wastewaters coming from the dyeing cycle of the tannery industry. The colour of the permeate waters depend on the effluent used. Colour rejection was always above 70% in the cases studied meaning that there is a possibility of using these waters as process waters in other baths. This, however, needs to be investigated.

14.2.13 Chromium (iii) salt recovery from tannery wastewater with microfiltration and ultrafiltration

It was shown that a combination of microfiltration and ultrafiltration produces a clean chromium salt (permeate) solution and allows at the same time to work with fluxes four to five times higher reducing the membrane area needed for ultrafiltration. According to the proposed process, a reduction of the sludges produced is expected which means a saving in the chromium recovery process costs.

14.2.14 Management of chrome compounds

It was shown that electrodialysis can be used to convert a spent chrome liquor into a nearly chrome-free sulphate liquor to be used as pickle solvent, and a chrome liquor with an adequately reduced sulphate content to be used as the main chrome tanning solution. This process, however, could be expensive.

14.2.15 New brine treatment plant reclaims pure salt and purifies wastewater

It was shown that brine obtained from the preservation of raw hides could be treated with a combination of centrifugation, vacuum evaporation, reverse osmosis and thermal treatment for salt and water recovery. The merits of this process should be investigated.

14.2.16 Evaluation of membrane technology for the treatment of tannery effluent in South Africa

Severe fouling of polysulphone UF membranes was experienced when the final effluent of a tannery (after physical/chemical pretreatment) was treated prior to RO desalination. However, it was demonstrated that it should be possible to control fouling with chemical cleaning. Membrane fouling was also experienced when the ultrafiltered effluent was treated in a RO unit. Fouling, however, could only be partly controlled and more work will be required to solve the problem. Good TDS removals were obtained with RO.

Poor results were obtained when soak paddle effluent was treated with RO. A salinity reduction of only 46,5% could be obtained. Low fluxes (75,5 ℓ/m^2.d) was obtained due to the fouling nature of the effluent.

Better results were obtained with the treatment of an effluent arising from the soak paddles, fleshing, splitting and deliming processes 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 appears that it should be possible to control membrane fouling with regular chemical cleaning.

Membrane fouling was experienced during the treatment of an ultrafiltered dyehouse effluent with RO. Electrical conductivity was reduced from 1 181 mS/m to 156 mS/m (86,8% removal).

It was shown that little membrane fouling took place when ultrafiltered liming effluent was treated with RO. The electrical conductivity of the RO feed was reduced from 654 to 154 mS/m (76,5% removal).

It was also shown that almost no fouling took place when ultrafiltered deliming effluent was treated with RO. The electrical conductivity was reduced from 1 017 mS/m to 349 mS/m (65,7% removal).

Reverse osmosis technology should be successfully used to desalinate tannery effluent if membrane fouling could be controlled. This should be achieved with proper pretreatment of the effluent prior to desalination. It was shown that a feedwater with an electrical conductivity in the range from 2 580 to 4 290 mS/m could be desalinated to conductivities in the range of 300 to 753 mS/m. The capital cost to treat 1 000 m^3/d of the final effluent produced by a tannery with a combination of UF and RO is estimated at R12,0 million (R5,4 million for tubular UF and R6,6 million for tubular RO). Spiral RO (R4,0 million), however, will reduce the capital cost to R9,4 million. Operating costs are estimated at R5,65/m3 for the tubular systems (R2,19/m^3 for UF and R4,10/m^3 for RO). Therefore, RO technology should be a suitable technology for the desalination of tannery effluent especially with the new generation of RO membranes.

14.2.17 Microfiltration, ultrafiltration and nanofiltration for salt and chromium recovery from spent and tanning/pickling effluent for reuse in South Africa

It was demonstrated that NF treatment of the MF permeate could remove approximately 55% of the organics from the MF permeate. Approximately 70% of the sodium chloride in the UF permeate could be recovered with NF. However, membrane fouling may be a problem. Good chromium removals (approximately 99%) could be obtained during neutralization of the spent tanning/pickling effluent prior to MF treatment. Consequently, this procedure could also be used for chromium and salt recovery from the effluent. The recovered chromium, however, after acid dissolution could be contaminated with organics.

14.2.18 Cleaner technology options

The following Cleaner technology options can be applied by tanneries for water and chemical savings and pollution control : -

(a) Salt free hide and skin preservation
(b) Mechanical desalting
(c) Counter current soaking
(d) Enzyme assisted soaking
(e) Green fleshing
(f) Enzymatic sulphide free unhairing
(g) Lime splitting
(h) Hair saving unhairing-liming
(i) Direct recycling of liming float
(j) Automatic water/chemical application
(k) Ammonia-free deliming agents such as carbon dioxide

(l) Chrome recovery, high chrome exhaustion and/or chrome liquid recycle
(m) Through-feed dyeing with spent dye liquor
(n) Reduction in water consumption by better housekeeping

Large savings can be obtained by implementing cleaner technologies at tanneries. The payback period for chromium recovery, for example, was estimated at 18 months.

14.2.19 Opinion of overseas and South African leather experts

Overseas leather experts are of the opinion that there are only a handful of membrane plants in operation overseas within the tanning sector, primarily in Italy and primarily for the treatment of process liquors for chemical recovery. Reverse osmosis and nanofiltration appears not to be applied at present although different groups are working on these technologies for potential application for effluent desalination and chemical recovery.

South African leather experts are of the opinion that salt pollution caused by the tannery industry should be addressed by the proper technology. Most of the South African leather experts are not very familiar with membrane technology as a tool for effluent treatment. However, membrane technology will be an acceptable technology for the treatment of tannery effluent once a track record has been established. At present membrane technology appears not to be economic for the treatment of tannery effluent due to the low charges for effluent disposal in the effluent disposal systems. However, there will be no choice as to treat tannery effluent with membrane technology when it becomes more expensive to discharge tannery effluent or when the effluent discharge standards become stricter. Also, tanneries might loose business if they do not comply with the requirements of the ISO 1400 Standards.

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16. APPENDICES

APPENDIX 1

MINUTES OF MEETING

Review Meeting		:	23/02/1999 10.30 hrs
PDU/2A – Pilot RO Unit		:	RePO-UNIDO Madras
Meeting called by :	AS	**Type of meeting:**	Review meeting with Aqua Chemicals & Systems Mfg. Ltd., & CLRI & RePO personnel on operation of pilot RO unit.
Attendees	Mr A Sahasranaman Mr K V Emmanuel	Mr Parthasarathy, Director, ACS.	Mr Ravindranath, Scientist, CLRI

Agenda : Review of operation of pilot RO unit at ATH tannery, Melvisharam

Discussion:

1. AS explained the purpose of the meeting was to identify the reason behind certain difficulties observed in the pilot RO unit at Melvisharam and to find out remedial measures for the unit. Certain observations made by RePO personnel and CLRI scientists during their visits to the site indicated that there were some reduction of the performance in the pilot RO unit of late. CLRI scientists also reported some irregularities in operation and monitoring of the system by ACS.

2. KVE briefly described the background of the present problem. During end of December, 1998 a certain dye which is very rarely used in the tannery appeared in the effluent and since the pretreatment was not effective (the hydrogen peroxide addition was suspended since June, 98 following failure of RO-1 membrane) and the operator of the plant did not stop the plant, the nanofilter (RO-1) membrane got choked completely. Subsequently recovery from nanofilters has come down and by mid January, the flow rate had become very low. ACS has replaced two cartridges (out of six) of nano filters and thereafter performance slightly improved. Now, the flow rate from RO-1 is only 1.2 m^3/hr as against designed level of 1.7 m^3/hr. This difficulty had produced a chain of problems such as intermittent operation of RO-2, increase of return flow and reject, increased pressure in RO-1, etc. The other points, though minor in comparison with the above, are the inadequate monitoring practice as observed by Mr. Aloy and also the non operation of some flow meters in the plant. Further, the promise to appoint a good operator from ACS was not yet fulfilled.

3. Mr Parthasarathy replied that the problem with the red dye was reported to the tannery management and warned them that this may cause serious problems with the membrane. But then the consensus was that since, the operation was coming to an end (so it was considered then), all permutation and combination involving all worse conditions could be tried out to find out possibility of damage to the membrane and hence the feeding was continued with the red dye. He mentioned that even now the ETP is not stabilized and the

TSS and colour of the treated effluent given to the inlet of RO is quite high. The TSS value at present is 250 – 300 mg/ℓ as against the assured value and though not specified in the agreement, the colour of the effluent was assumed to be pale yellow and the present reddish dark colour is quite high.

4. KVE mentioned that the ETP is now getting stabilised again and the tannery has been advised for some remedial measures such as polishing chemical treatment, etc. to improve the situation. The sensible idea to deal with residual colour is to bring back efficient pre-treatment (re-installation of controlled peroxide dosage may be considered). If ACS has any specific suggestions to improve the performance of the ETP, the same also will be considered.

5. AS asked Mr. Parthasarathy for his honest view about the viability of RO technology for tannery effluent from the experience so far in which ACS had also invested considerably. Mr. Parthasarathy mentioned that he is confident that RO can be successfully employed for tannery effluent provided some improved pre-treatment measures are designed for future installations, so that the system will take care of even unexpected components like the red dye. Further the pre-treatment should be designed site specific. He was confident that up to 80% recovery is not difficult.

6. KVE and Mr Ravindranath felt that it would be more reasonable to assume the recovery to be in the range of 70 – 75% only.

7. The main complaint of Mr Ravindranath was the non reliability of data provided by the new operator at the site. The same observation was made by RePO/Mr Aloy earlier and during the last meeting Mr Parthasarathy had assured to replace the present operator, but this was not carried out till now.

8. Mr. Parathasrathy stressed that ACS is equally interested in obtaining reliable and true data which will be helpful for their future project design, etc. Following the last meeting, the operator recommended by RePO was called back from another site to be posted at ATH, but he met with a severe accident and had to be hospitalized. The efforts to call back another engineer who is senior and acceptable to RePO are on and Mr Parthasarathy assured AS that this will be done within a weeks time.

9. Regarding the problem with nanofiltration, Mr Parthasarathy mentioned that replacement of nanocartridge will be a costly affair (four cartridges may cost minimum Rs. 100,000). KVE was of the opinion that replacement of these cartridges is the solution to continue the operation effectively. The other less preferable option would be to increase the operating hours of nanofilter to operate the RO

Conclusions & Recommendations

4. KVE, Mr Ravindranath and Mr Parthasarathy will visit the site on 24 Feb 1999 for detailed inspection of the system, particularly the nanofilter.

5. Further action points will be listed once the detailed examination is completed.

Additional Information

Distribution : AS/MA/KVE/ACS/CLRI

File: PDU 2A

APPENDIX 2

Annex-2
Inspection Report to Pilot RO unit at ATH Tannery, Melvisharam on 25 February, 1999

Background

The pilot RO unit was working satisfactorily till the end of December 1998 when a certain dye used in the tannery manufacturing process had reportedly fouled the RO-1 (nanofilter) membrane which resulted in difficulties in the operation pattern. Certain other observations, mostly in monitoring of the pilot unit was made by RePO experts, Mr. Aloy and CLRI. To discuss all these observations and firm up a further course of action for regular operation of the system during the remainder of the subcontract period, AS had called for a meeting on 23 February, 1999 with Director of Aqua Chemicals. During the meeting it was decided that Mr. Parthasarathy, Director of ACS should visit the site and inspect the unit in detail in presence of UNIDO and CLRI representatives.

Accordingly the visit to the site was made on 25 February '99 and the salient observations made are enclosed in this report.

Participants

1. Mr T. Parthasarathy, Director, Aqua Chemicals & System Mfg. Ltd., Chennai
2. Mr E. Ravindranath, Scientist, CLRI, Chennai
3. Mr K.V. Emmanuel, National Expert-Env. Engg., RePO, UNIDO.

Objectives

1. To review the operation critically, particularly with respect to RO-1.
2. To plan suitable improvement measures to overcome difficulties identified in the operation.
3. To plan for 24 hour operation for a short period with designed TDS level of 8 000 mg/ℓ.

Details of inspection done

The team visited the project site and spent the day at the pilot unit, inspecting all components critically.

Altogether the operation seemed normal, except for the comparatively low yield from nanofilter (RO-1). The system was being operated for 8 hours and during the period

20 December, 1988 to 25 February, 1999, it had to be stopped two times due to the pressure rise in RO-1 which was an outcome of blockage of RO-1 when the red dye had appeared in the effluent.

Areas of improvement identified:

1. The flow meter in the reject line was not giving correct readings. This was explained by the supplier as due to the very low flow rate (less than 150 lph) in this line. As this measurement is a vital component, it was decided that the entire rejects (approximately 1 200 litres per day) will be collected in a masonry tank of 6 000 litres capacity recently constructed using a flexible hose. A wooden scale with measurement in centimeters will be placed in this tank and the level in the tank will be measured on a daily basis. This also will be helpful in collecting composite sample of the reject.

2. The flow meter removed from the reject line will be installed in the incoming raw water line by ACS.

3. A new log sheet incorporating start and stop timing of all sections of the RO unit will be prepared and maintained for better counter checking of the flow pattern, etc. RePO will provide a model log sheet – Deadline: 10 March 99.

4. All flow meters installed in the plant will be re-calibrated and installed back by ACS.

5. As Mr Parthasarathy did not favour the re-installation of hydrogen peroxide dosing at the photochemical oxidiser, the present treatment with no peroxide dosing will continue.

6. Since utilizing concentrate for backwashing of filters resulted in difficulty in computing mass balance of salts, a new backwashing strategy was considered. At present, the flow to the raw water collection tank is stopped by around 5.45 P.M. and only the re-circulated reject water from RO-1 and RO-2 was accumulated in the raw water collection tank (RWT) and inlet water tank (IWT) which is used for further pumping to IST-1. Once the feeding to the RO is stopped and flushed, the water remaining in RWT and IWT is used for backwashing of the MGF, ACF and Softener. This backwash water containing a considerable quantify of TDS, creates confusion in mass balancing in monitoring of the system. The following arrangement was decided for avoiding this difficulty: Once the membranes are flushed, the water remaining in the RWT/IWT will be pumped through the pre-treatment units and will be collected in the IST-1. Fresh raw water will be used for backwashing of the filters and the backwash water will be sent back to the ETP. This backwash will be analysed for mass balancing of TSS, COD, etc. The only risk

associated with this operation is that the inlet TDS would be quite high (around 25-30 gpl) in the morning. However, RO-1 is capable of withstanding this TDS and secondly when the feeding to RO-1 starts, the incoming input water from the ETP will dilute the TDS level to 15-20 gpl. After trials, if required, storage of this water in barrels and controlled addition may be considered.

7. The water used for membrane flushing will not be discharged. It will be either mixed with permeate for end use or sent back to the collection tank.

8. After the inspection of the system, Mr Parthasarathy was confident that by aggressive cleaning of nano-membranes normality may be restored. Hence it was suggested that a shutdown of operation should be done, nano membranes taken out, cleaned thoroughly using speciality chemicals, installed back and operated for two days to see if the membranes would be fully functional. If the output of the RO could be regained to the tune of 90%, the same membrane could be used for continued operation with a modified flow pattern which will be provided by ACS. If this was possible, the membranes will have to be imported which may take 3 – 4 weeks time and till such time the system will be operated with a modified flow pattern. The cost of imported membrane is estimated at Rs. 100 000/-

9. A one week trial of 24 hour operation using inlet water of 8 000 mg/ℓ TDS was considered. Since there was no surety about the timings of the tannery starting processing of raw hides & skins, the following arrangement was suggested: About 10 tanker loads of treated effluent from Melvisharam CETP (Vishtec) could be transported (in two days during the week) and collected in the old aeration tank of ATH. The required quantity of treated effluent from ATH will be mixed with this effluent to have a combined TDS of 8 000 – 9 000 mg/ℓ. The pilot unit will then be operated for one week (24 hours a day) and composite samples will be collected for analysis. ATH will provide for cleaning of the tank and transportation of effluent from Vishtec. Necessary manpower during the continuous operation will be provided by ATH.

10. An experienced operator will be placed at the site ASAP. Mr Parthsarathy will confirm this appointment by 1st March, 99.

11. For improvement of treatment plant of ATH, additional polishing treatment will be considered. KVE will provide a sample of poly aluminium chloride to ATH and Mr Iqbal will conduct trials using the chemical to reduce colour and TSS further. Regular application of this treatment will be ensured by ATH.

Action points & schedule

Action by ACS

#	Action	Target date	Status as on 30 April 1999
1	Starting inspection of nano (RO-1) membranes	1 March 99	Done
2	Detailed inspection & cleaning of membrane	5 March 99	Done
3	Re-calibration and installation of flow meters	5 March 99	Done
4	Installation of reject flow meter in inlet line	5 March 99	Done
5	Back washing modifications	8 March 99	Done
6	Appointing an experienced operator	8 March 99	Done
7	Operation of pilot until 24 hrs for one week		After replacement of nano membrane

Actions by ATH

#	Action	Target date	Status
1	Lab studies & Improvement measures in ETP	1 March 99	Done
2	Arranging for reject collection in Masonry tank	2 March 99	Done
3	Cleaning of old aeration tank	2 March 99	Done
4	Arrange for effluent transport from Vishtech CETP		After replacement of nano membrane
5	Co-ordination of 24 hrs operation		

Actions by RePO, UNIDO

#	Action	Target date	Remarks
1	Providing chemical samples for Lab studies to ATH	1 March 99	Done
2	Providing new formats of log sheets	10 March 99	Done
3	Follow up of the above schedules	Continuous	

Actions by CLRI

#	Action	Target date	Remarks
1	Arrangement for composite sampling during continuous operation		After replacement of nanomembranes

APPENDIX 3

The capacities, recoveries and cost breakdown to treat 1 000 m^3/d of the final effluent produced by a tannery are as follows : -

Tubular UF

• Feed	1 000 m^3/d
• Recovery	80%
• Permeate flow	800 m^3/d
• Retentate flow	200 m^3/d
• Flux	300 ℓmd
• Feed pressure	6 bar

Tubular RO

• Feed	800 m^3/d
• Recovery	75%
• Permeate flow	600 m^3/d
• Brine flow	200 m^3/d
•	200 ℓmd
• Feed pressure	35 bar

The capital cost for the two tubular systems are estimated as follows : -

• Tubular UF	R5,4 million
• Tubular RO	R6,6 million

Note: The cost of spiral RO will be about 60% of the cost of a tubular system.

The respective operating costs (excluding redemption of capital and maintenance) are estimated as follows : -

Tubular UF

• Pretreatment & CIP chemicals	R0,36/m^3
• Energy	R0,14/m^3
• Sponge ball replacement	R0,04/m^3
• Membrane replacement	R1,65/m^3

This gives a total estimated operating cost of R2,19/m^3 permeate for UF.

Tubular RO

• Pretreatment and CIP chemicals	R0,44/m^3
• Energy	R0,95/m^3
• Sponge ball replacement	R0,04/m^3
• Membrane replacement	R2,75/m^3

This gives a total estimated operating cost of R4,00/m^3 permeate for RO.

Other related WRC reports available:

The extraction of ionic and chemical species from water by membrane extraction

Smit JJ • Koekemoer LR • van Wyk AM

In this project the extraction of polluting heavy metals and other chemicals from a feed solution through a membrane into a strip solution was investigated, using supported liquid membranes. This concept comprises a capsule containing the so-called strip solution, impregnated with the correct extractant which would effect the extraction.

The extraction of nickel with suitably formed membrane capsules gave extraction rates and total extraction values which were dependent on the following five variables:

- Temperature
- Speed of agitation on the feed side (Reynolds number)
- Acid concentration in the strip (inside) solution
- Special ligand concentration in the feed-side solution
- Extractant concentration in the membrane.

Each of the variables increased the extraction rate and the combined nett effect was an increase of at least 100 times greater extraction than reported in literature. Furthermore, an empirical rate equation was developed which yielded a polynomial expression in terms of all the independent variables mentioned. This rate equation is a powerful tool to predict and determine the required size of a plant using this technology.

Report Number: 761/1/98 **ISBN: 1 86845 393 6**

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