



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

July 1998

US/RAS/92/120

**Regional Programme for pollution control in the tanning industry
in South East Asia**

**ULTRAFILTRATION APPLICATION IN TANNERY WASTE WATER
TREATMENT**

Prepared by

Mladen Bosnic
UNIDO Consultant in tannery effluent treatment
(US/RAS/92/120/11-62)

In cooperation with

S. Rajamani
Technical Expert: UNIDO - Regional Programme Office
&

A. Sahasranaman
Programme Coordinator: UNIDO - Regional Programme Office

Project Manager

Jakov Buljan
Agro-industries and Sectoral Support Branch

This paper has not been edited

The views presented are those of the authors and are not necessarily shared by UNIDO

References herein to any specific commercial product, process, or manufacturer do not necessarily constitute or imply its endorsement or recommendation by UNIDO.

TABLE OF CONTENTS

Part I	Executive Summary	1 – 3
Part II	Report on the study travel to Zenon b.v., Arendonk b.v. & Lederfabriek P. Driesen, The Netherlands by Mladen Bosnic, TEH Projekt, Croatia	1 – 13
Part III	Conclusion on preliminary study by Dr. S. Rajamani, RePO, UNIDO, Chennai	1 – 3

PART I

EXECUTIVE SUMMARY

EXECUTIVE SUMMARY

Conventional tannery effluent treatment process if properly designed, conducted and operated succeed in reducing many of the pollutants present in the tannery effluent. Significant reduction of 90% or more can be seen in BOD₅, COD, chromium and suspended solids.

Conventional processes however are not designed to treat TDS including chlorides. Also unless special arrangements are made, the nitrogen content of the effluent is not specifically addressed.

The environment authorities in many countries have set standards for pollutant discharge with respect to total dissolved solids and / or chlorides as well as nitrogen (expressed as TKN or NH₃ (or both)) in several countries for surface water and sometimes also sewer discharge. Whilst these standards naturally vary from country to country and often within each country, standards, which have been set, can and will not be achieved by conventional treatment processes. The reason already given is that conventional treatment processes are not designed for significant reduction in TDS, chloride and nitrogen levels in the effluent. Also, in view of the world wide practice of preservation of hides and skins through wet salting, salt laden streams are generated in the tanning industry which are well above these standards. The main source of (ammonical) nitrogen is from the deliming process. For this a technically feasible alternative is available. Viz., CO₂ deliming which may or may not be commercially viable depending on many factors including cost and availability of CO₂.

UNIDO through its Regional Programme for pollution control in the tanning industry has been actively looking for solutions to improve conventional treatment processes which simultaneously address the nitrogen in the effluent and give the possibility of addressing TDS / chloride in the effluent. Currently the following technologies relating to TDS and / or nitrogen in effluent are implemented or being implemented in pilot demonstration units: (i) mechanical / manual removal of excess salt from wet salted hides and skins (2) reverse osmosis of treated tannery effluent units: (3) improved solar evaporation, (4) under a different project CO₂ deliming in a small scale tannery addressing alternative to ammonical nitrogen, (5) wet land treatment system using reed bed possibly resulting in nitrification / denitrification (6) another technology which has been under consideration is the multistage evaporation system to recover salt from tannery effluent (7) ultra filtration. This report deals specifically with ultra filtration as being offered by Zenon BV Netherlands through Arendonk BV Netherlands.

A preliminary study had been conducted on the suitability of ultra filtration for treatment of tannery effluent and as replacement for secondary clarifier in the treatment process (Mladen Bosnic, UNIDO consultant in tannery effluent treatment, December, 1997). This report provides some basic information and has been included as Part II.

The report contains 3 Sections and 1 Annex with leaflets. The system uses membrane technology for separation of treated effluent from activated sludge instead of conventionally used settling tanks or dissolved air flotation system. Thus the ultra filtration system has been integrated in the effluent treatment plant. This process has been patented under the name ZenoGem ®. Separation of the activated sludge from the treated effluent is carried out either by pressure ultra filtration or through under pressure (vacuum) micro filtration (patented process with hollow fibre membrane, ZeeWeed ®).

It is reported that the ZeeWeed under pressure system is much more economical than pressure UF system (energy saving due to lower pressure 0.2 bar versus normal 3-4 bar is approx. 80%), but was not tested yet in tannery effluent treatment plants.

The ZenoGem ® system, on the other hand, is operational for instance in Dreisen tannery, Dongen, the Netherlands. The report prepared by the UNIDO consultant gives full details. The tannery at present processes about 12 tonnes wet salted raw hides, 5 tonnes split and 5 tonnes wet blue per week. Effluent being discharged is 30 – 40 m³/day with COD of 25000 – 30000 mg/l, BOD₅ 9000 – 10000 mg/l, TKN of 800 – 900 mg/l, chlorides 7800 mg/l and sulphates of 4700 mg/l.

After screening 5 mm, equalisation, fine screening, chemical treatment the overflow is pumped into a bioreactor made in concrete and divided into 2 concentric zones. At this stage the COD in the effluent is 12000 – 15000 mg/l and TKN 700 – 800 mg/l. In the 125 m³ zone a fine bubble aeration system has been installed, whereas a mechanical stirring system has been installed at the 90 m³ anoxic zone (for denitrification). Hydraulic retention time in the bioreactors is about 6 days and 500 m³/h of pressurized air (after cooling) is used for oxidation. MLSS level inside the tank is maintained at 60000 mg/l and pH at 7 (if need be through additional chemicals).

The ultra filtration system operates at 6.2 bar (initial pressure) to 3.8 bar (pressure drop membrane). The diameter is 12 – 13 mm with a capacity of 90 l/m² per hour. Expected life span of membrane is 3.5 years (2.5 years in operation at present). After this final effluent has COD 900 mg/l, BOD₅ < 5 mg/l, TKN 30 – 40 mg/l and is discharged into the municipal sewer for further treatment. The sludge being produced in the ultra filtration is 3 – 4 m³/day (10% of original volume), whereas the excess (wasted) sludge is maximum 1 to 1.5 tonnes per week (approx. 0.1 – 0.2 tonnes dry solids).

The ultra filtration system allows high levels of mixed liquor suspended solids in the aeration tanks of 30000 – 60000 mg/l, as compared to the more conventional 2500 – 5000 mg/l. Longer retention time of larger molecules and more micro-biological activity positively influence reduction in BOD₅, suspended solids and organic COD.

The high MLSS maintained in the system also acts as a safeguard against shock loading and possible presence of toxic elements in the effluent. Furthermore, the system can be halted for some time (for example, it had been once stopped for four weeks) unlike any conventional treatment system, the microorganisms still surviving.

The quantity of sludge generated is lower than in conventional biological treatment systems. The small reactor volume reduces the area requirements.

Part III of the report is the independent technical evaluation of the system by UNIDO's Regional Programme Office in Chennai, India. Many of the concerns raised above have been reiterated.

Furthermore the evaluation highlights the already mentioned likely operational difficulties that are likely and US \$ 500,000. Also it requires good operational control and frequent cleaning of membranes (once every week in NaOCl and NaOH).

It has been stated that in many tannery effluent treatment plants relatively good results are being achieved with conventional systems and since these are operational it may not be very attractive to modify the entire biological system to accommodate this type of treatment system. This is especially the case in those treatment plants where fixed aerators have been installed in the biological systems, which do not allow for required level variation.

Due to high MLSS levels maintained oxygen requirement will be high which is likely to offset gains made in energy saving due to the smaller sized bioreactor tank.

Whilst it is recognised that the system is patented, theoretically it may be possible to further modify the membranes to enable it to tackle TDS, chlorides, etc.

In conclusion, application of ultra filtration in combination with revised biological reactor may in the current situation not be attractive in the region. However when a new effluent treatment plant is planned under of the projects this option will be taken into account. The attached report is a good guidance and reference material.

PART II

**REPORT ON THE STUDY TRAVEL TO ZENON b.v., ARENDONK b.v. &
LEDERFABRIK P. DRIESEN, THE NETHERLANDS**



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

December 1997

US/RAS/92/120

Regional Programme for pollution control in the tanning industry
in South-East Asia

Report on the

**STUDY TOUR TRAVEL TO ZENON b.v., ARENDONK b.v. &
LEDERFABRIEK P. DRIESEN, THE NETHERLANDS**

(02 – 03 December 1997)

Prepared by

Mladen Bosnic
UNIDO Consultant in tannery effluent treatment
(US/RAS/92/120/11-62)

Project Manager

Jakov Buljan
Agro-industries and Sectoral Support Branch

This paper has not been edited

The views presented are those of the authors and are not necessarily shared by UNIDO

References herein to any specific commercial product, process, or manufacturer do not necessarily constitute or imply its endorsement or recommendation by UNIDO

INTRODUCTION

UNIDO ISED/AGRO - LEATHER (SIDO Mr. J. Buljan) noticed an article in the journal "WORLD LEATHER", November 1995, prepared by ZENON ENVIRONMENTAL b.v. Netherlands (marketed by Arendonk, Netherlands), concerning their process named ZenoGem®, or the application of the membrane technology (ultrafiltration (UF)) in the (tannery) waste water treatment (used instead of the secondary settling, for the separation of the activated sludge from the biologically treated effluent).

This new method was estimated as very interesting and very promising, specially for the obtaining of the very high level of the quality of the treated effluent, especially for suspended solids (SS), BOD₅ and COD.

It was also estimated that this method can be maybe also used for the (partially) disburdening of the some overloaded secondary settling tanks and to produce so better quality of the treated effluent (specially concerning the SS and with SS connected BOD₅).

Some supplement information concerning ZenoGem® were also collected through Mr. R. Daniels.

SIDO Mr. Buljan has requested Arendonk International b.v. (as marketing organisation for the application of the ZenoGem® process in the tanning sector) for the more precise information and for the (tentative) general quotation for the (pilot) effluent treatment plant (ETP). The problem of the "total dissolved salts" (TDS) in the effluent was also mentioned.

Arendonk gave the general quotation for ETP, capacity 120 m³/d (or average 5 m³/h) for Hfl. 980.000 (their letter ref.: 3082B961001, File Nr.: 960195 - ref. 96003001/cs - 604111, dated 15.03.1996 with attached process description and equipment specification). In this quotation the problem of TDS in the effluent was not mentioned.

On the 25.02.1997 Mr. P. van Arendonk (the owner of the Arendonk International b.v.) visited UNIDO Vienna and informed Mr. Buljan on the following:

- Zenon has installed two new ETP using the same technology (one in Spain and one in Belgium).
- prices of membranes have significantly decreased
- instead of using pressure, their latest models use underpressure (vacuum)
- Arendonk is very interested to supply a pilot (industrial scale, say 100 m³/d) unit for demonstration purpose under RAS programme at a special price
- (as also previous suggested) Arendonk invited UNIDO again to visit the plant
- they are also interesting for the solution of the TDS problem in the effluent

This visit was confirmed by Mr. Buljan's fax to Arendonk, dated 03.03.1997, with the typical values of raw composite effluent, treated effluent and standards concerning tanning industry and the underlined problem of the TDS for many tanneries.

Zenon confirmed through their fax ref. 9703102/cs, dated 24.03.1997, the contact between UNIDO, Arendonk and themselves, and also their interest in the participation in such projects

and to supply UNIDO with the requested information and also suggested to visit them and their installation in Netherlands.

In meantime UNIDO was also informed that some other company (for example Babcock - Wabag Esmil dealing with effluent treatment) have the similar system for the extraction of the treated water from the activated sludge tank. Mr. Frendrup collected also some information of the ETP in a tannery in Germany having the similar treatment process with pressure UF system, constructed by a German company.

Finally UNIDO has organised the visit to Zenon, Arendonk and Lederfabriek P. Driesen in Netherlands on 02. and 03.12.1997 and has sent Mr. Willy Frendrup, Dansk Teknologisk Institute, Denmark and Mr. Mladen Bosnia, effluent treatment consultant, Croatia to collect the necessary information at the site and to give the comments and suggestion through the appropriate report.

2. FINDINGS

2.1. ZENON ENVIRONMENTAL b.v.

The meeting with the Zenon's representative Mr. Alex Geraci, Sales Department was held in Hotel Die Port van Cleve in Amsterdam on 02.12.1997.

Zenon Environmental Inc. is a Canadian company with approx. 400 employees.

Offices in Europe are in Netherlands (8 employers), Germany (12 employers), Italy (5 employers) and Hungary (approx. 30 employers (feeding water preparation for the power stations)).

Their marketing company for the application of the membrane technology in the tanning industry in the Europe is Arendonk, Netherlands.

The main activities are in the field of the water and wastewater treatment with membrane technology for the production of drinking water converting brackish water and seawater for municipalities in the fixed installations, for the military operations and emergencies in the mobile modular units, for the production of pure or ultrapure water for different use (power plants, pharmaceutical and biotechnology companies, electronic industry, etc.) and for the wastewater treatment for municipalities, waste landfill leachates and many industries, including tanneries.

They are also dealing with the use of the membrane technology in the some industrial processes.

Zenon produce themselves two types of membranes: tube and hollow fibre, and only for UF and microfiltration. The material is polymer. The other types of membranes or the membranes for other processes they are buying on the world market. They do not sell separately their membrane, than only the complete (water and wastewater) treatment systems.

One of the special application of the membrane technology is in the biological wastewater treatment, for the separation of the treated effluent from the activated, instead of conventional used settling tanks (or sometime also dissolved air flotation (DAF)).

This method is patented under the name ZenoGem®.

The separation of the activated sludge from the treated effluent is carried-out either by pressure UF, or underpressure (vacuum) microfiltration (patented process with hollow fibre membrane under the name ZeeWeed®. The ZeeWeed® underpressure (vacuum) system is much more economic than pressure UF system (energy saving for water extraction is approx. 80 %), but was not tested yet in the tannery ETPs. Their opinion is that this system could also be applied in the tannery ETPs.

They installed approx. 200 such installation to today (We asked for reference list, but they did not have it). For the municipal wastewater treatment, they installed approx. 80 ETPs in Canada and 1 in Germany. The maximum ETP capacity for municipal effluent was up to 2 - 3.000 people equivalents (P.E.). Other ETPs are for industrial and other effluents.

Zenon have not the prices for the separate process components or for the complete (non-defined) units, but they are ready to give quotation for the complete ETP system on the concrete requirement.

General opinion of Mr. Geraci is that this can not be cheaper than conventional system and should be apply only if other advantages of this system are interesting.

They estimate that the life time of membranes for UF can be approx. 4 years for the optimum operation conditions. They estimate also that the prices of the membranes are approx. only 10 % of total investment costs and it means that the appreciation costs per year, only for membranes, are approx. 2,5 % of total investment costs in the equipment.

In the tanning sector they installed 2 ETP to today (Lederfabriek P. Driesen, Dongen, Netherlands and Jules V. Paermentier (production of "chamois" (glass (windows) cleaning lather)), Oeselgem, Belgium.

All these ETPs are with pressure UF. The inlet pressure is approx. 6 - 7 bars, outlet pressure approx. 3 - 4 bars, and head losses approx. 3 - 4 bars. The velocity in the UF modules is approx. 4 - 5 m/s. The flux through the membrane is approx. 50 - 70 l/m².h (max. 100 l/m².h).

ETP at Paermentier is designed only for the treatment of carbonaceous organic load (COD), and the ETP at Lederfabriek P. Driesen also for nitrification (< 1 mg/l of ammoniacal-N) and partial denitrification (in this tannery approx. 90 % of the tanning is vegetable).

Nitrification is carried-out in the biological aeration tank, and denitrification in separate (or part of the same) tank without aeration and with mechanical mixing.

Aeration in the biological reactor is by submersible fine bubbles diffusers (aerators) and blowers. The desired concentration of MLSS in the biological reactor is 30 - 35 g/l for tubular membranes (pressure UF system) and 20 - 25 g/l for hollow fibre membrane (underpressure (vacuum) microfiltration system ZeeWeed®).

During the start-up and fine tuning of the ETP at Lederfabriek P. Driesen, they had many problems. Due to the membrane technology of the separation of the activated sludge from the treated effluent and much different conditions in the biological reactor compared with the conventional system, the activated sludge is completely different. The calculation methods of the biological reactor can also not be the same as for conventional activated sludge.

The first pre-treatment system consisted only of a relative coarse screen (approx. 5 mm Aquagard®) and so inadequate (concerning the SS) pre-treated effluent was treated in the ZenoGem® system. This provoked many problem in the functioning of the membrane system and their premature clogging and wearing-out. For this reason they up-graded the pre-treatment system by installation of fine screen and settling tank to reduce the SS to 100 - 300 mg/l at the inlet to ZenoGem® system.

Having the experience with the ETP at Lederfabriek P. Driesen, Zenon considers their quotation to UNIDO for the pilot plant, dated 15.03.97 as not complete and not technical correct, because of the suggested insufficient pre-treatment.

If the previous quotation for pilot plant of 120 m³/d, or 5 m³/h is not acceptable for UNIDO, because of high costs (was quoted for Hfl. 980.000) Zenon is ready to quote the very small pilot plant for the rent, capacity of approx. 1 - 2 m³/d, complete with nitrification and denitrification and UF. The condition for this rent is that the pilot plant should be operated by their staff.

Mr. Geraci thinks that it is quite possible to put their ZeeWeed® modules in the existed activated sludge aeration tank to improve the biological process and discharge the existed secondary settling tank (directly, by smaller flow and indirectly, by higher concentration of activated sludge in the aeration tank). These modules need some supplement compressed air (for sludge blowing) and this air can be taken from existed compressed air system (from blowers). They are also ready to give quotation for such modification, but are not ready to give one module to be separately tested somewhere in South-East Asia.

Some other question were also discussed with Mr. Geraci:

- The excess sludge quantity can be controlled by sludge age. For the very long sludge age it can be practically zero, but it is not recommended because of too high concentration of MLSS and problems with the accumulation of some "toxic" components in the activated sludge
- If the pure oxygen is used for the aeration (oxygenation), instead of air, they do not expect directly the better results, but it can maybe be useful if the necessary quantity of the oxygen can not be supplied by oxygenation by air.
- They do not suggest to use activated carbon simultaneous in the biological process, because it can have the negative influence on the membrane system. If necessary, they suggest to use the activated carbon as tertiary (supplement) treatment.

Zenon tested in Lederfabriek P. Driesen for two months also the process of the TDS elimination from the treated effluent for the reuse in the tannery. For these tests they used RO and nano-filtration. The results were good

Zenon's opinion (as also our) is that the greatest problem is what to do with concentrate. They do not have better solution than evaporate or burn it, but both of this methods are very expensive.

2.2. LEDERFABRIEK P. DRIESEN, Dongen

We visited the Lederfabriek P. Driesen, Dongen on 03.12.1997, accompanied by Mr. Alex Vos, Sales Manager Arendonk.

The host for our visit was Mr. Gerard Driesen, Managing Director Lederfabriek P. Driesen. Mr. Gerard Driesen gave as many very useful information concerning the installation, operation and problems of ETP, but was not able to give the detailed information concerning the concrete results of ETP operation. The chief of the effluent treatment plant (ETP) Mr. Renederen,

environmental engineer, deep involved in all details, was absent and Mr. Gerard Driesen promised to send us this information by mail after his return.

This tannery produce the finish lather mainly from raw cow wet salted hides (approx. 12 t/week), and partly from split (approx. 5 t/week) and from wet blue (approx. 5 t/week). Total capacity is approx. 22 t/week, or approx. 4 - 5 t/working day.

90 % of tanning is vegetable.

Lederfabriek P. Driesen have also two more tanneries, but these are only for dry operations and all wet operation are in the visited tannery.

The tannery management understood very early that the water is the most expensive "chemical" in the tannery.

The tannery should pay for water by multiple ways:

- payment to water authority for raw water consumption
- the costs of process water preparation
- the costs of wastewater treatment
- payment for waste water discharge

For example, the tannery should pay approx. the following amounts only for the water discharge depending of the effluent treatment:

- Hfl. 800 - 900.000/year for the non-treated effluent
- Hfl. 150 - 200.000/year for primary treated effluent
- Hfl. approx. 25.000/year for the biologically treated effluent (as it is now)

The process water supply is by the pumping of underground water and its treatment (iron, manganese). The designed water consumption was 120 - 140 m³/d, but with water saving measures, they reduced the consumption to approx. 30 - 40 m³/d (for example they are using now the treated effluent for all equipment and tannery floors washings).

The treated effluent is discharged into Dongen sewerage system and is treated once more through their communal ETP. The contribution of tannery's effluent in the total quantity of the communal effluent is very small (< 1 %), and the relatively very high COD concentration of the treated tannery effluent is not problem. Final discharge from communal ETP is in the small river Dongen (before the construction of communal ETP, this river was very polluted (with very unpleasant smelt), but now the fishes are living in this river).

They think, that they are now, with the water consumption of approx. 10 m³/t of hides, at the lower limit and that this so low consumption is maybe not to good for the lather processing.

They also made the two months tests with RO to recycle the treated effluent. The test results concerning the water quality were very good (they produced practically the pure potable water), but the main problem was the rest (concentrate). They have also a very interesting idea to use this salted concentrate for the roads/ways treatment during the winter for the freezing protection, but the problem was the concentration of other components of concentrate and the

concentrate storage (normally not the idea for India!). Other idea is to send this concentrate to the sea by pipeline (a pipeline exists from an other not far tannery to the sea; approx. 100 km!). The price of the RO plant is estimated on Hfl. 300.000. For this moment they did not decide to install this treatment, because they estimate this solution non economic.

The (Zenon's) ETP started in 1994 and consist of:

- tannery sewerage system (no separation of the streams; only common effluent)
- self-cleaning coarse screening (Aquagard, approx. 0,5 m wide, 5 mm opening)
- equalisation tank (horizontal tank approx. 50 m³; obviously existed) (mixing with air)
- self-cleaning fine screening (Rotostrainer, 0,5 mm opening, with brush-cleaning; without water) (installed later, due to the problems with SS)
- treatment with polyelectrolytes
- vertical hopper bottom settling tank (approx. ø 2,5 m; capacity 15 m³ (installed later, due to the problems with SS)
- equalisation tank (horizontal tank approx. 120 m³; obviously existed) (mixing by recirculation by pumping)
- biological reactor divided into two concentric compartments:
 - internal compartment for denitrification, capacity approx. 90 m³ (with mechanical mixing)
 - external compartment for aeration, capacity approx. 125 m³ (with bottom aerators)
- accessories to biological reactor:
 - compressed air system (Roots type blowers and air coolers; the air cooling was installed later, because the very high temperature (approx. 48°C) in biological reactor did not permit the efficacious denitrification)
 - antifoam dosing system
 - sometime the polyphosphate dosing
- UF system for activated sludge recycling, consisting of:
 - tube membranes ø approx. 1/2" working under pressure of approx. 6,2 bars and head drop 3,8 bars, average flux 90 l/m².h
 - helicoidal screw pumps
 - chemical cleaning system (sodium hydroxide and sodium hypochlorite)
- sludge dewatering, consisting of Netzsch chamber filter press 800 x 800 mm, with 64 plates, cake volume approx. 850 l, filtration cycle 3 - 4 h, approx. 2 filtration cycle/d
- Control system for the completely automatic operation of the ETP consisting of: D.O., pH, temperature, levels, flow and some other measurings, Datalogger, Computer and alarm system with different alarm levels (some responsables are alarming also automatically at home during non-working time for some very important alarms)
- good equipped laboratory for the ETP control and testing of the different streams in the tannery for the better understanding of the possibility of each step in the effluent treatment and the source of the pollution. They verify their laboratory results with the exchange of the samples with some other laboratories. This laboratory is also use for the students education and praxis

During the start-up and the operation of the ETP (especially in the fist 1 - 1,5 year) many problems appeared and was solved:

- inadequate pre-treatment and to high concentration of SS in the inflow to bioreactor;

this problem was solved by installation of fine screening and settling tank

- underestimated oxygen (air) consumption; the capacity of the blowers was changed from approx. 80 Nm³/h to 500 Nm³/h
- too high temperature in the reactor, due to the hot compressed air from blowers and reaction heat; this problem was solved by cooling of the compressed air (from approx. 95°C to 25°C) after blowers and so the temperature in the reactor was decreased from approx. 48°C to approx. 37°C. The cooling (hot) water is used in the tanning process.
- too high concentration of MLSS in reactor (> 100 g/l) in some periods due to the too high concentration of SS in the inflow to the reactor and not sufficient extraction of excess activated sludge. This provoked some membrane clogging. Although Zenon designed and suggested the MLSS concentration of 30 - 35 g/l, they found as optimum and they are working with approx. 60 g/l.
- problem in the nitrification/denitrification, due to the very high temperature in the reactor. This problem was solved by air cooling and better control in reactor in the last 9 months and the nitrification/denitrification process is now acceptable.
- in the periods when they were working practically without denitrification it was necessary to adjust the pH value with sodium hydroxide.
- problem with the pump sealing and the necessity to change the sealing once per month. They are using now the double sealing with the oil bath between these two seals and the results are much better.

The ETP has the following results:

- the average treatment result are presented in the following table:

Parameter	Raw effluent	1. step of treatment	Biological treatment
COD mg/l	25.000 - 30.000	12.000 - 15.000	500 - 900
BOD, mg/l	9.000 - 10.000	2.000 - 3000	< 5
Kjeldahl-N mg/l	800 - 900	700 - 800	30 - 40
Ammoniacal-N mg/l			< 1
Nitrates-N mg/l			50 - 100

Note: Before the stabilisation of denitrification process the content of nitrates-N was approx. 500 mg/l.

- the final effluent is really very clear, but is coloured light brown
- the quantity of excess activated sludge is estimated at 1 - 1,5 t/week as is treated together with primary sludge
- total sludge production is estimated at 18 t/week of sludge cake with 35 - 40 % of DS. In my opinion this quantity is some too high, and maybe can be some misunderstanding, because this do not correspond with the information concerning the filter press (two filtration cycles/day, each approx. 850 l (can correspond approx. to 1 t of cake/cycle),

it means approx. 10 t of cake/week of 5 working days)

- the sludge cake with approx. 5000 mg of Cr/t of DS is disposed on the landfill
- they estimate the membrane life time to 2,5 - 3 years

As stated during the visit, non sulphide oxidation before the biological treatment; their opinion is that this are not necessary and the existed concentration of the sulphide (> 100 mg/l) can not negatively influence the biological process and all the sulphide will be oxidise during this process.

They informed us that the oxygen concentration in the reactor is 10 - 12 mg O₂/l, but in my opinion it should be some misunderstanding, because it is quite not possible because the saturation level of the dissolved oxygen in the water at this temperature (37°C) is much lower.

We stated the very unpleasant smelt of ammoniac in the filter press room. While the room is closed (and probable adequate ventilated) no remarkable smelt out of the sludge filtration room.

They had stopped also sometime the tannery for the longer time (up to 4 weeks) and the ETP was working without effluent and they did not have the problem to restart the normal operation after the restart of the tannery.

They follow the market of the membranes and they have made some test with the membranes of other producing companies and have stated the similar results.

2.3. ARENDONK INTERNATIONAL, Tannery Machines b.v., Goirle

The Arendonk's representative Mr. Alex Vos, Sales Manager accompanied us to the Lederfabriek P. Driesen, Dongen on 03.12.1997.

After the visit to Lederfabriek P. Driesen we had a meeting on 03.12.1997 at Arendonk headquarter in Goirle with Mr. Johan van den Hoven, Director and Mr. Alex Vos, Sales Manager.

We repeated our interest to be informed in details on the membrane technologies applied in the tanning industry and tannery ETPs, as the ZenoGem® for the biological treatment of the tannery effluent and possible up-grading of the existed conventional activated sludge biological treatment with ZeeWeed® modules, so for the solution of the TDS problem in the treated effluent and to test all these membrane technologies.

They promised to see all these questions once more with Zenon and to give us adequate information and quotations.

We visited also their workshops for the reparation of the used tannery machinery and some store of the repaired machines.

They informed us that the prices of general repaired machines are approximately 55 - 60 % of the new machines.

Mr. Frentrup collected also their leaflets for tannery machines.

3. SOME CONCLUSIONS AND SUGGESTION FOR THE FUTURE ACTIVITIES

According to the previous information and the results of the study travel the conclusions are:

- The up-grading of the conventional activated sludge process by membrane technology for the separation of the treated effluent from the activated sludge, instead of secondary settling (or maybe flotation) have many advantage:
 - the quality of the treated effluent concerning the SS and BOD₅ is much better (both the SS and BOD₅ are < 5 mg/l)
 - the quality of the treated effluent concerning the COD and some organic components should be also better, due to the retaining of larger molecule longer time in the process
 - possibility to have very high concentration of MLSS (20.000 - 25.000 mg/l for underpressure modules ZeeWeed® (microfiltration) and 30.000 - 35.000 (and more) mg/l for pressure UF) in the biological reactor reduce the hydraulic retention time and size of installation
 - due to very high concentration of MLSS the process is very resistant to loading shocks and toxic components
 - very reduced quantity of excess activated sludge
- The disadvantage are:
 - sensitive to the SS solids overloading (pre-treatment should reduce the SS content to some 100 mg/l)
 - relatively higher investment and operational costs in comparison with conventional activated sludge process (up to today applied only for special cases whit very high quality demands, special industry difficult to treat wastewater and the smaller quantity of effluent)(with the decrease of the membrane prices this technology will be more and more nearer to the conventional technology
 - relatively high technology needing educated staff
- With membrane technology (RO, nanofiltration) it is possible to reduce quite economically (depending on the local situation) the TDS content in treated effluent to the acceptable level, but no the economical solution for the problem of the concentrate treatment or disposal. If no possibility to dispose the concentrate the only solution are to evaporate or burn it, but the price for these treatments could be grater than for the treatment by membrane technology.

Some suggestion for the future activities are:

- Follow all the information concerning application of the membrane technology in the tanning industry and tannery ETPs, as for the application of the membrane process in the modified activated sludge process for the treated effluent separation, so for the

solution of the TDS problem

- Collect the quotations from Zenon/Arendonk for pilot plant for ZenoGem® process and if possible also for the testing of the ZeeWeed® module in the existed activated sludge biological treatment
- Try to have the quotations for the similar process from other companies (for example: Babcock Esmil, or the company which installed the similar system in Germany (by Mr. Frendrup)
- Collect the quotation from Zenon/Arendonk and from other companies dealing with membrane technology for the solution of the problem of TDS in treated effluent. From the same companies, or from some other specialised companies ask the suggestion and/or quotation for the solution of the problem of the concentrate, resting after the effluent treatment by membrane technology
- According the collected and selected quotation organise the testing of membrane technologies in the tanneries and tannery ETPs

PART III

CONCLUSION ON PRELIMINARY STUDY BY DR. S. RAJAMANI, RePO, UNIDO

CONCLUSION ON PRELIMINARY STUDY BY DR. S. RAJAMANI, RePO, UNIDO

Ref: Report on the study travel to Zenon b.v. Arendonk b.v. & Lederfabriek P. Driesen, The Netherlands (December 1997), based on the work of Mr. Mladen Bosnic, UNIDO Consultant.

1. BACKGROUND

Conventional effluent treatment system used for treatment of tannery effluent consists of physico-chemical treatment for the removal of colloidal suspended particles followed by biological treatment for the removal of dissolved organics.

The biological treatment generally comprises of one or multiple stage aeration units. Activated sludge treatment is the most commonly adopted biological treatment system for the tannery effluent treatment. In conventional activated sludge treatment the effluent is aerated in an aeration basin to develop and create favourable environment for the growth of biomass and the effluent flows to the settling tank after aeration where the biomass is collected in concentration in the settled form and re-circulated into the aeration tank to maintain the required MLSS. This is an integral part of activated sludge treatment, since the efficiency of the settling tank determines the maintenance of effective activated biomass in the activated sludge treatment. But in this system not all the biomass could be collected and re-circulated to the aeration basin and some amount of biomass with suspended solids is discharged in the supernatant from secondary settling tank with residual solids and often the treated effluent is turbid.

To improve the biomass concentration and activity in aeration tank the conventional secondary settling tank system by an ultra filtration unit which retains the biomass inside the aeration system while allowing better filtered effluent to flow out from aeration tank. The physical arrangement required to eliminate the settling tank and adopt ultra filtration unit comprises of ultra filtration membrane and pipelines to carry back the reject from the ultra filtration unit (with all biomass) into the aeration tank. In order to select and adopt appropriate cost effective technologies for treatment of tannery effluent, UNIDO under its Regional Programme for South East Asia has been exploring the feasibility of this option. This system has been successfully tried on tannery effluent in The Netherlands, and its performance evaluation was done by Mr. M. Bosnic, UNIDO consultant.

2. MERITS OF THE SYSTEM

The system requires less land space as the ultra filtration unit is much smaller compared to the conventional settling tank / clarifier. In addition, aeration tank volume also can be reduced by increasing the concentration of MLSS.

Since total MLSS concentration is retained within the aeration system it is possible to increase the concentration of MSS to very high levels (25000 – 30000 mg/l) as against conventional MLSS concentration of 3000 – 4000 mg/l. Due to the build up of MLSS in this system it is possible to reduce the size of aeration tank, though the aeration capacity required remains the same.

The conventional settling tank produces fairly good quality effluent clear from suspended solids, but the levels of suspended solids and turbidity depend on the operational conditions and have been observed to be in the range of 50 – 100 mg/l. By using ultra filtration unit, the effluent practically can be free from all suspended solids and therefore clarity would be comparatively better.

Due to the reduction of suspended solids in the treated effluent the BOD, COD would also be comparatively less. Good reduction of organics and colour can be anticipated in the system using ultra filtration.

The system will be helpful against the shock loads or toxicity due to high MLSS concentration in the aeration system.

Since large amount of biomass is retained within the aeration tank ensuring sufficient feed for microorganisms, it is possible to operate biological treatment intermittently with break in feeding, which is not possible in conventional aeration system.

It is possible to get better nitrification in the system aided with ultra filtration.

The sludge from aeration system aided with ultra filtration system would be better mineralised due to better endogenous respiration, which mean less quantity as well as less putrescibility of waste bio-sludge.

This system would be more suitable if the treated effluent is to be further treated in a system like reverse osmosis for reuse of water and minimise the preconditioning units required for reverse osmosis.

3. DEMERITS OF THE SYSTEM

The ultra filtration system is a high tech operation and requires specific monitoring capability. This system is generally not available in developing countries, owing to the low priority assigned to effluent treatment plants by the industry.

The operation of ultra filtration system necessitates installation of additional aeration systems allowing level variation in aeration tanks. This means the aeration systems adopted should be either diffused aeration or floating aeration system. Many of the effluent treatment plants available in some South East Asian region utilise the fixed type aerators in the aeration tanks.

The very high concentration of MLSS retained in the system requires high mixing and oxygenation power. So there will not be any change in the total power consumption, mixing and oxygenation power for the specific capacity suitable for new units and replacing the existing system may not be attractive.

Retention of all bio solids in the system results in accumulation of toxicity, which could make some problem in the treatment when the MLSS levels increased beyond a certain level.

The conventional settling tanks is a rugged and common treatment easy to operate and maintain. The ultra filtration system requires special care for operation and maintenance.

The life of ultra filtration membrane would be around 2 – 3 years requiring periodical replacement of membrane and this adds to the operation cost.

4. CONSIDERATIONS

The technology though comparatively advanced, one of the possible future locations for application of this could be in India.

Almost all working ETPs in India in the tannery sector are achieving relatively good quality of treated effluent in the conventional treatment systems. As such the interest for such a treatment modification may not be attractive to the industry at present.

The treatment system combined with ultra filtration technology presupposes low inlet suspended solids to the aeration tank. In many of the effluent treatment plants in India the suspended solids concentration in the raw effluent has been observed to be very high and very few effluent treatment plants are achieving the prescribed suspended solids level of 100 mg/l in the outlet of chemical treatment.

Most of the tanneries in India have already established effluent treatment plants and most of them are using surface aerators for aeration tanks and with this set up, it may not be attractive to opt for the system. Hence, the replicability of this PDU is low in the current situation.

The oxygen requirement for effective operation of aeration systems combined with ultra filtration systems is very high and the high temperature prevailing in this area may adversely affect the intake of oxygen in the system.

The operational expertise presently available in the region is not very high even in India. A sophisticated system like ultra filtration requires skilled manpower training, constant attention and maintenance.

At the moment the membrane price is high and the conventional treatment may be more economical.

5. CONCLUSIONS

Considering the present situation in South East Asia region, this advanced technology appears to be ahead of its time for the tannery sector. In future when enforcement authorities insist on the treated effluent quality requirement including parameter like COD, TDS, etc. this technology may be found attractive. At this stage a pilot demonstration unit of this type may be considered in future probably linking the Reverse Osmosis system when adopted for recovery of quality water.

In the present circumstances, it is recommended to consider this PDU under second phase of RAS programme and for the present PDU/2C may be closed and the report may be filed for future reference.