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This report "Some Challenges in the Treatment of Tannery Effluents" was prepared by Jakov Buljan and S. G. Rajamani

#### 1. MASS BALANCE AND SOURCES OF POLLUTION IN A TRADITIONAL TANNERY

Leather manufacture is a water-intensive process and generates a significant volume of liquid and solid waste. The main reason is that the only true leather-building substance in raw hide is corium collagen, everything else (hair, epidermis, fat, some proteinaceous matter etc.) has to be removed. To achieve these goals substantial quantities of both general and specialty chemicals are needed. Again, due to inherent characteristics of physical-chemical processes applied, the major part of them is not actually used up and ends as waste to be discharged. Untreated liquid, solid and to some extent air emissions generated by the tanning industry can thus pose a serious threat to the environment, particularly to surface and ground water.

The schematic tannery operation and sources of pollution are shown in Figure 1.

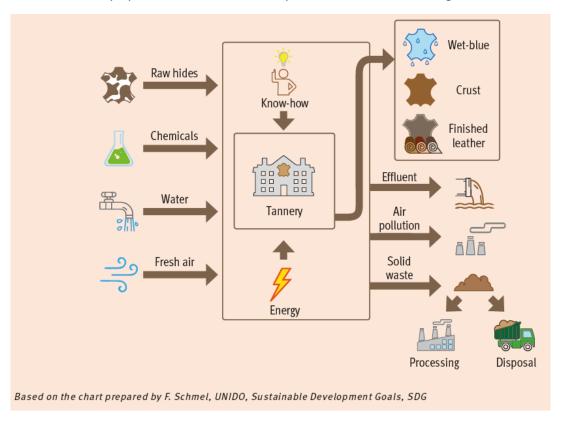


Figure 1. A simplified schematic chart of the tanning operations

# 1.1. Collagen

When evaluating the efficiency of leather manufacture, it is quite sobering to realize that only some 50 % of the corium collagen, the only true leather-building substance, ends up as leather. Details of collagen distribution in finished leather and solid waste is given in the following table.

Table 1. Collagen distribution: wet salted hide, finished leather and solid waste (Starting material: 1,000 kg wet salted European raw hides, avg. 25.6 kg/piece, splitting in chrome)

Component	Amount of collagen*				
	kg % of corium collagen % of total collagen				
Input					
Corium collagen (Leather building collagen)	280	100	92		

Component	Amount of collagen*		
Subcutis collagen	24	-	8
Total collagen input	304	-	100
Output			
Grain leather	113	40.0	37.2
Split leather	36	13.0	11.8
Total collagen in finished leather	149	53.0	49.0
Total collagen in solid waste (shavings, trimmings etc.)	155	47.0	51.0
Total collagen output	304	100	100

<sup>\*</sup>Note the distinction between the **corium collagen** and **total collagen** (corium plus subcutis/flesh collagen).

## 1.2. Mass balance of chemicals in leather processing

General chemicals (acids, bases, salts) are required in leather process to create the medium for reactions but are not actually absorbed. Finishing products are essential to lend the desired appearance. The mass balance of chemicals in leather process is given in the following table.

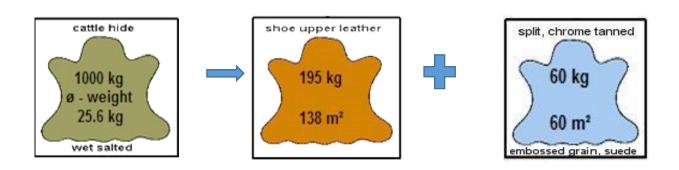
kg/ton of wet salted hide Chemicals Added in process in/on leather & splits Wasted Chrome extract 101 19 82 (Cr<sub>2</sub>O<sub>3</sub>)(25)(12)(13)Organic tannins 25 20 5 Fatliquors 22 17 5 Dyestuffs 5 4 1 Acids, bases, salts 191 191 Tensides 3 3 Enzymes 5 5 Finishing products 100 12 88 452 Total 72 380

Table 2. An example of mass balance in leather processing

Note: EU (BREF 2013) figures about chemicals addition are even higher.

# 1.3. Approximate weight and area proportions, light European hides

In case of processing one tonne of wet salted raw hides results in approximately 138 m<sup>2</sup> of finished (shoe upper) leather and some 60 m<sup>2</sup> of chrome tanned splits that can also be turned into leathers of acceptable quality (embossed grain, suede) as shown in the following diagrams.



## 1.4. The scope for and limitations of cleaner technologies

Pollution prevention, which ultimately leads to lower treatment costs, remains the supreme priority. By applying industrially proven low-waste advanced methods such as the use of salt-free preserved raw hides and skins, hair-save liming, low-ammonia or ammonia-free deliming and bating, advanced chrome management systems, etc., it is possible to significantly decrease the nature and amount of emissions as shown in the following figure.

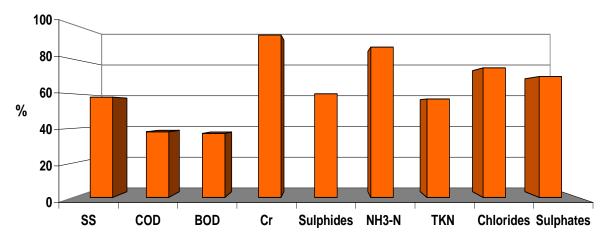


Chart by M. Bosnić

Figure 2. An estimate of decrease of pollution loads in wastewater after introducing advanced technologies, %

It means that despite all preventive measures, there is still a considerable amount of pollution load to be dealt with by the end-of-pipe methods.

Contrary to widespread misperception that vegetable tanning is environmentally harmless (in reality its effluent has very high, difficult to treat COD) and that is why we here deal only with chrome tanning because it is by far the most prevailing leather tanning method.

Effluent treatment is a complex process and requires specialists for planning, designing and operating them. However, it is important for tanners to acquaint themselves with the main pollutants, their impact on environment and the basic principles and prevailing methods of tannery effluent treatment. That makes them better equipped for a dialogue with the factory's own environmental unit, wastewater treatment specialists as well as with environmental authorities and NGOs.

## 2. POLLUTION PARAMETERS – DESCRIPTION, ENVIRONMENTAL IMPACT, LEGISLATION

The effect of excessive pollutant levels commonly found in tannery effluents can be severe, their impact is here described for general guidance. Also, there is no single measure of pollution load; a few key parameters considered together are needed to offer a reasonably accurate picture.

Table 3. The main pollution parameters: description, environmental impact

Parameter	Description	Environmental impact
Biochemical Oxygen Demand, BOD <sub>5</sub>	The quantity of oxygen required during the stabilisation of decomposable organic and oxidizable inorganic matter by aerobic biological action under standard conditions over five days.	The greater the BOD, the lower the amount of dissolved oxygen available for aquatic life.
Chemical Oxygen Demand, COD	The quantity of oxygen consumed for the total oxidation of the oxidizable matter (organic and inorganic) with dichromate as the oxidising agent.	Depletion of oxygen available for aquatic life, including chemical compounds not easily degraded by microorganisms normally present in the water recipient.
Total Suspended Solids, TSS	Made up of solids of two distinct characteristics: Solids with a rapid settling rate (settleable solids) and semi-colloidal solids.	Substances present in the TSS significantly contribute to the BOD & COD levels. Responsible for sludge generated in the course of effluent treatment.
Chromium, Cr <sup>3+</sup> (III)	Emanates from the incomplete uptake of chrome salts used for tanning - from technical, economic and environmental aspect the most superior method of leather making. Discharged from processes in soluble form; however, precipitates and stabilized colloids are formed.	Very fine, chrome stabilized colloids are also formed; partially tanned protein solids are highly resistant to biological breakdown. Also, chromium hydroxide precipitates and persists in the ecosystems. Regrettably, often confused with potentially more hazardous Cr <sup>6+</sup> (VI) form.
Sulphide, S <sup>2-</sup>	Results from the use of sodium sulphide and sodium hydrosulphide and from the breakdown of hair in the unhairing process. At the pH below 9.5, hydrogen sulphide gas evolves. Strict segregation of alkaline and acidic streams essential. Characterised by the smell of rotten eggs but, very unfortunately, only at lower concentrations.	Flammable, corrosive, highly irritating gas. Mixtures with air may explode violently. Low concentration induces headaches and nausea. At higher levels, death sets literally within seconds. The most frequent cause of fatalities in the tanning industry. If discharged to surface water, even in low concentrations very toxic.
Total Kjeldahl Nitrogen, TKN	A widely accepted measure of presence of nitrogen in effluent: it includes both the organic nitrogen (i.e. nitrogen contained in amino acids/proteinaceous compounds) and nitrogen present in ammonium salts. Being inert, atmospheric nitrogen dissolved in water is not included.	Excessive growth of plants and algae, clogging of waterways, flows impaired. As the plants die their decomposition leads to depletion of oxygen and ultimately to anaerobic conditions and bad smell.
Chlorides (CI) <sup>-</sup>	Originate from the large quantities of common salt used in hide & skin preservation and/or in the pickling process. Highly soluble and stable, unaffected by effluent treatment.	Excessive concentrations inhibit the growth of plants, bacteria and fish in surface waters. Also, increased salt content in groundwater is now becoming a serious environmental hazard.

Parameter	Description	Environmental impact
Sulphates, (SO <sub>4</sub> ) <sup>2-</sup>	Emanate from the chrome tanning salts, sulphuric acid, ammonium sulphate and some retanning agents; from sulphide removal by oxidation & use of alum sulphate in the coagulation process.	Remain as sulphates or are broken down by anaerobic bacteria to produce the toxic, corrosive and malodorous hydrogen sulphide. Contribute to TDS.
Oil and grease	Released from within the skin structure; some fatliquors are added as lubricants for desired feel as well as some water repellence.	Oil and floating grease agglomerate to form 'mats' causing blockage problems. Thin layers on water surface significantly reduce oxygen transfer from the atmosphere.
Total Dissolved Solids (TDS)	Indicate the amount of all inorganic and organic substances dissolved in wastewater; essentially, everything present in water other than pure H <sub>2</sub> O and suspended solids. In the tannery effluents, the main relevant components are <b>sulphates</b> and <b>chlorides</b> . Colloquially referred to as salinity.	High TDS concentrations exert varying degrees of osmotic pressures and make otherwise fully treated wastewater unfit for irrigation and livestock watering; also, high TDS often becomes lethal to the biological inhabitants of an aquatic environment. Not affected by the usual effluent treatment.
рН	Quantitative measure of the acidity or basicity of aqueous or other liquid solutions. The scale on which 7 is neutral, lower values are acidic, higher values alkaline.	Both highly acidic and highly alkaline values negatively affect the flora and fauna of the receiving water bodies.

# Remark:

The effect of excessive pollutant levels commonly found in tannery effluents can be severe; their impact is here described for general guidance. Also, there is no single measure of pollution load; a few key parameters considered together are needed to offer a reasonably accurate picture.

#### 2.1 Sources of Pollution

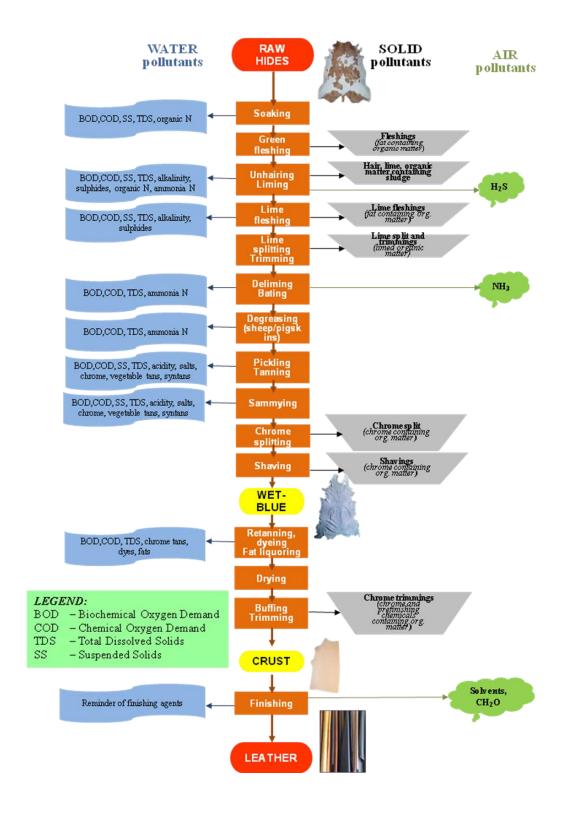


Figure 3. The main points of waste discharge along the leather making process

To avoid possible confusion arising due to differences in water consumption it is practical to indicate the amount of pollutants generated per tonne of raw hide input. While generally lower water consumption is very desirable (nowadays in well managed tanneries significantly below 30 m³/tonne) it obviously results in considerably higher concentration of pollutants.

The characteristics of the wastewater discharge from conventional process is given below:

Table 4. An example of pollution load, conventional process

Parameter	Typical pollution load, conventional process kg/tonne of wet salted hide	A tannery with daily input of 10 tonnes of w.s. hides, every day discharges approx. (kg)
Volume of wastewater	30 m³/tonne	300 m <sup>3</sup>
COD	180	1800
BOD <sub>5</sub>	90	900
Suspended solids (SS)	120	1200
Cr <sup>3+</sup>	5	50
S <sup>2-</sup>	5	50
Total Nitrogen (TKN)	14	140
Cl <sup>-</sup>	180	1800
(SO <sub>4</sub> ) <sup>2-</sup>	80	800
Oil and grease	10	100
TDS *	400	4000
рН	6 - 9	

<sup>\*</sup> The main constituents of the TDS are chlorides (Cl) and sulphates ( $SO_4^{2-}$ )

# 2.2. Legislation

The average pollution load from raw to finishing process with water consumption of 45m<sup>3</sup>/tonne is given in the following table.

Table 5. An example of the average total pollution load - water consumption of 45 m³/tonne\*

Parameter	Unit	Average total pollution load	Typical limits, surface waters
BOD <sub>5</sub>	mg O <sub>2</sub> /I	2000	30 – 40
COD	mg O <sub>2</sub> /I	4000	125 – 250
Suspended solids SS)	mg/l	2000	35 – 100
Cr <sup>3+</sup>	mg Cr/l	150	1.5 – 2.0
S <sup>2-</sup>	mg S/I	160	1.0 – 2.0
Total Nitrogen (TKN)	mg N/l	280	100
Cl <sup>-</sup>	mg CI/I	5000	Locally specific
SO <sub>4</sub> <sup>2-</sup>	mg SO <sub>4</sub> /I	1400	Locally specific
Oil and grease	mg/l	130	Locally specific
TDS	mg/l	10000	Locally specific
рН		6 - 9	5.5 – 9.5

<sup>\*</sup>Nowadays already nearly halved, typically 20-25 m³/tonne

#### 2.3. Banned substances in tannery effluents

In addition to the controlling of traditional parameters such as COD, BOD<sub>5</sub>, TKN, chrome, sulphide etc. an important trend in European legislation is stricter regulation of the presence of biocides and pesticides in tannery effluents such as DDT, hexachlorohexane, aldrin, dieldrin, endrin, isodrin, naphthalene etc.: some prohibited substances, notably organochlorine compounds, are stable enough to survive wastewater treatment process. Only registered and approved degradable biocides can be used and their choice is becoming more and more limited.

Virtually all pesticides found in the tannery wastewater are residues of pesticides used to treat live animals whereas biocides are regularly used in preservation and soaking, pickling, tanning and post-tanning processes.

# 3. EFFLUENT TREATMENT, TYPICAL TREATMENT STAGES

Wastewater treatment is a multi-stage process to purify wastewater before it enters a body of water, is applied to the land or reused. The goal is to reduce or remove organic matter, solids, nutrients, chrome and other pollutants from wastewater, the receiving body of water can cope with as established by relevant authorities. Before turning to treatment, it is important to emphasise:

- Design of an effluent treatment plant (ETP) is always tailored to requirements of a specific site; thus, there are no two identical ETPs.
- Since matter can be neither created nor vanish, pollutants contained in effluent cannot disappear; they are only converted into environmentally more acceptable or easier to dispose form (sludge).
- Somewhat paradoxically, obvious is often overlooked: the same amount of pollutants at lower water consumption means lower hydraulic load (volume) but higher concentration, not always easy to treat.
- It is important for a tanner who emanates wastewater, to understand the relation between the leather process technologies and wastewater treatment in order to reduce the overall cost of treatment.

The three main categories of tannery wastewater, each of very distinctive characteristics, are:

- Effluent emanating from the beamhouse liming, deliming/bating, water from fleshing and splitting machines; they contain sulphide, their pH is high, but they are chrome-free.
- Effluent emanating from the tanyard tanning and retanning, sammying; high Cr content, acidic.
- Soaking and other general effluent, mainly from the post-tanning operations fatliquoring, dyeing; low Cr content.

# 3.1. Segregation of tannery streams

The segregation of sectional streams and separate in-house pre-treatment are necessary for an efficient effluent treatment system. A typical tannery layout with locations of segregation and treatment are shown in following figure.

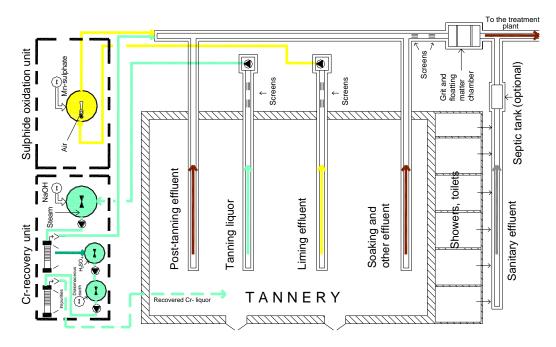


Figure 4. Schematic lay-out of the in-house segregation of streams, including chrome recycling and oxidation of sulphide in liming effluent

It is very important to segregate these streams and to pre-treat them separately respecting their characteristics to avoid possible safety risks (formation of deadly hydrogen sulphide) and to reduce cost of treatment and sludge disposal (to avoid contamination of sludge with Cr). In other words, mixing of liming and tanning streams gives rise not only to obnoxious smell typical for poorly managed tanneries: the resulting lethally poisonous gas hydrogen sulphide (H<sub>2</sub>S) is still by far the most frequent killer in tannery accidents, mainly in inadequately ventilated spaces, especially in pits and channels. Accordingly, the practice of "delegating" sulphide oxidation to the CETP homogenization tank is questionable.

The volume and pollution load of sanitary wastewater is comparatively insignificant.

Somewhat arbitrarily, it is common to distinguish the following main stages of effluent treatment:

- On-site treatment
- Physical chemical treatment (primary)
- Biological treatment (secondary)
- Advanced (tertiary) treatment
- Sludge handling & disposal

#### 3.2. On-site treatment:

Typically, in the case of CETPs servicing tannery clusters often found in developing countries, it is essential to have pre-treatment units installed in individual tanneries before the effluent is discharged into collection network. Their role is to remove large particles, sand/grit and grease but also to significantly reduce the content of chrome and sulphides.

The typical pre-treatment system for sulphide oxidation and chrome recovery system are shown in the following figure.

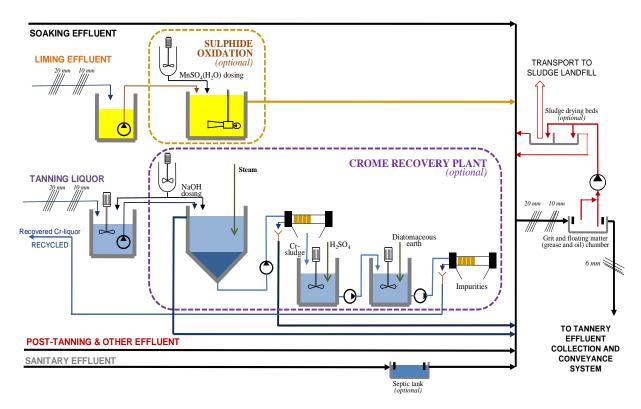


Figure 5. Schematic flow-chart of the in-house segregation of streams, chrome recycling, treatment of liming effluents and pre-treatment of mixed effluent in individual tanneries

# 4. PHYSICAL - CHEMICAL TREATMENT (PRIMARY)

Objectives:

- To eliminate the coarse material normally present in the raw wastewater that could clog/block pumps, pipes and, possibly, sewer lines
- To well mix & balance different tannery streams and thus produce homogenised "raw material" that can be treated in a constant way
- To adjust pH and eliminate toxic substances (sulphides) and/or shock loads that could negatively affect the rather sensitive biological treatment
- To significantly decrease the BOD/COD load and thus reduce the cost of and simplify the biological treatment phase.

The basic steps of the primary treatment are:

- Screening (bar, self-cleaning screens)
- Pumping/lifting, fine screening
- Equalisation & homogenization
- Chemical treatment (coagulation, flocculation)
- Solids separation, sludge dewatering

Quite often grease and sand trap is also included, usually before fine screening and pumping.

# 4.1. Screening

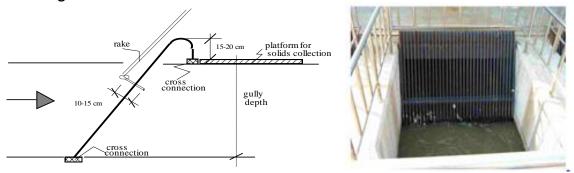


Figure 6. Bar screen, side view

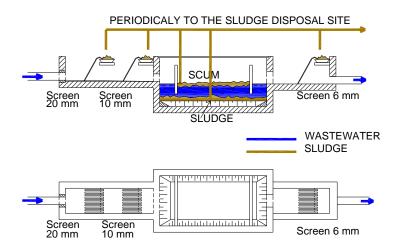


Figure 7. Simple, non-aerated grit and floating matter removal chamber

Large ETPs require more sophisticated, aerated arrangements for removal of grit and floating matter as shown in the following figure.

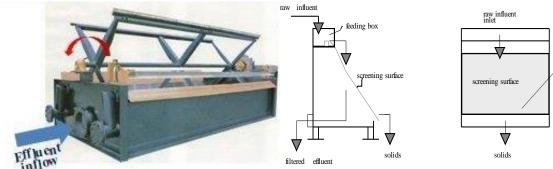


Figure 8. Self-cleaning, rotary brushes screen, Parkwood typeSelf-cleaning screen, Hydrosieve type

It is not possible to transfer effluents throughout the ETP by gravity only, at least one or more pumping/lifting stations are needed, the first typically located before the rotary screen. Depending on specific requirements – capacity/flow different types of pumps are used. Small and medium scale ETPs generally rely on different models of submersible pumps as shown below:

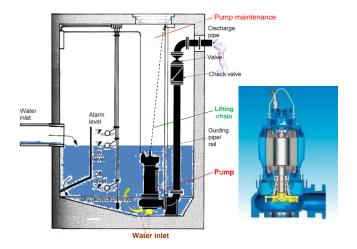


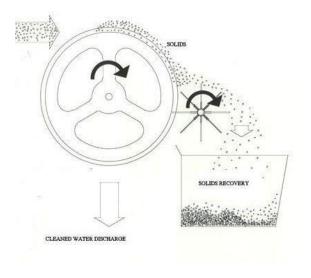
Figure 9. Submersible pump

For large volumes screw (Archimedes) pumps are preferred.



Figure 10. Archimedes type lifting pumps

Fine screening should drastically reduce the amount of fine suspended solids. Here are shown rotary drum type screens with outer and inner flow as shown in the following figures.





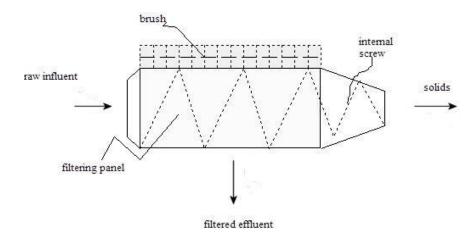


Figure 11. Rotary drum fine screen, outer and inner flow

#### 4.2. Equalization – Homogenization

The main aim is the homogenization and subsequently a steady flow of the balanced effluent for further treatment. Accordingly, the volume of the equalization tank normally corresponds to the total daily effluent discharge; at the same time, volumes of raw and treated effluent are more or less equal. Also, normally there is no significant temperature difference between raw and treated effluent.

It is very important to keep all particulate matters in suspension, i.e. to avoiding settling of solids. This is achieved by using mixing cum aeration devices such as diffused air systems, Venturi ejectors and fixed or floating aerators (lately avoided due to lower efficiency and problem of aerosols). In practice, to play safe, the volume of the equalization tank approximately corresponds to the total daily effluent discharge plus minimum storage requirement in the equalization tank for mixing-cum-aeration. A typical view of the equalization-cumhomogenization tank is given below:

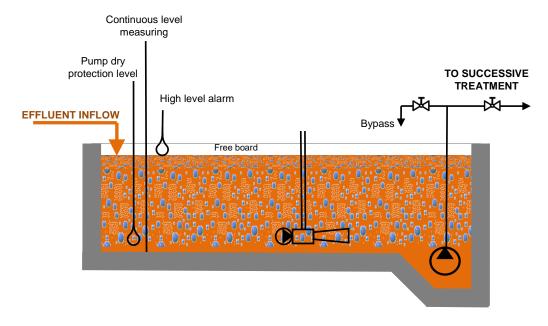


Figure 12. Schematic view of the equalization - homogenization tank

The energy required to keep the solids in suspension is some 50 Watts/m<sup>3</sup>, which is also sufficient for any residual sulphide oxidation.

# 4.3. Chemical treatment (coagulation, flocculation)

Chemicals are added in order to improve and accelerate the settling of suspended solids, especially of the fine and colloidal matter.

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart; as a result, the particles collide to form larger particles (flocs). Industrial aluminium sulphate (alum) is most commonly used coagulation agent but iron sulphate, iron chloride and lime are also used. Obviously, there is a side effect: coagulation agents add to the effluent's TDS load.

Polymers added during the flocculation stage help forming the bridges among the flocs and bind the particles into large agglomerates or clumps, which are then removed from the liquid by sedimentation, filtration, straining or floatation as shown in the following figure.

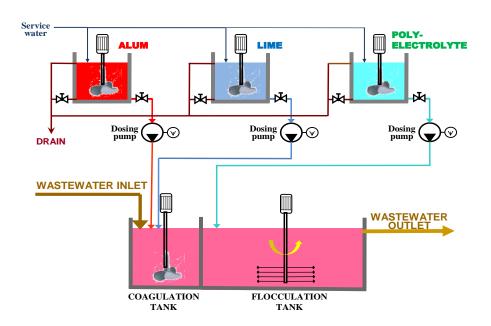


Figure 13. Schematic view of the coagulation and flocculation system

#### 4.4. Solids separation – primary sedimentation

The main objective is removal of suspended solids; various floatables like fats, waxes, mineral oils, floating nonfatty materials etc. ("grease"), not already removed in the grit and oil chamber (usually positioned between screening and equalization) are also separated here.

Primary settling tanks (clarifiers) are circular (more common) or rectangular with arrangements for continuous, quiet in- and out-flow, grease (scum) removal at the top and sludge removal at the bottom. The key design parameters are detention time (usually 1–2 hours), surface hydraulic loading (typically  $1 - 2 \, \text{m}^3/\text{m}^2$  per hour) and surface solids rate; the latest is expressed in kg/m² indicating the quantity of SS crossing the surface area of the tank over a certain time span (hour, day). Mechanical device (scraper) is necessary in larger settling tanks as shown in the following figure.

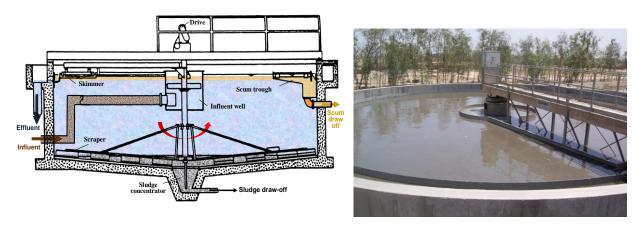


Figure 14. Schematic cross-section view & external view of a typical circular sedimentation

In some cases, mainly due to space shortage, solids are removed by flotation, usually by the Dissolved Air Flotation (DAF) system as shown below:

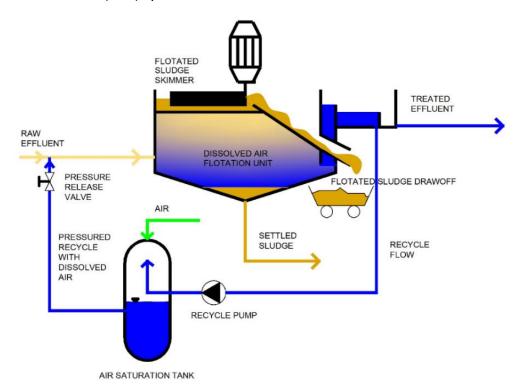


Figure 15. Schematic view of the Dissolved Air Flotation (DAF) unit

# 4.4.1.Sludge dewatering<sup>1</sup>

The sludge drawn from the bottom of the tank is in the form of slurry with dry solids (DS) content of only 2-4 %. For its evacuation special, progressing cavity type pumps as shown in the following figure are used.

<sup>&</sup>lt;sup>1</sup> The main part of sludge stems from the physical-chemical (primary) treatment and that is why it is described at this point.

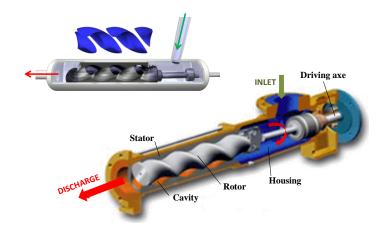


Figure 16. Schematic cross-section view of a progressing cavity pump type for sludge transfer

Further reduction of the water content is achieved in sludge thickeners (very much like circular clarifiers) followed by mechanical dewatering in plate filter presses, belt filter presses or decanter centrifuges. In addition to power and chemicals requirements, the key parameter for equipment selection is the achievable dry matter content in the dewatered sludge lowering the cost of its transport and disposal.

The construction of the sludge thickener is in practice identical with that of sedimentator although in some cases the Dortmund type with self-desludging slopes is also used as shown in the following figures.

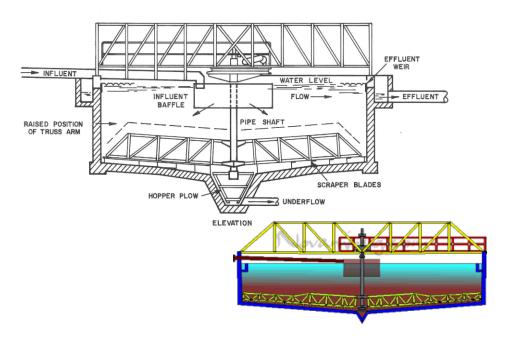


Figure 17. Schematic cross-section view of the gravity thickener



Figure 18. Recessed plate filter press with container for dewatered sludge

Through increase of dewatering level, improvement of wear and tear resistance (especially in the case of sludges containing fine sand) as well as by lowering the irritating noise, centrifuges have succeeded in conquering a lot of ground in dewatering tannery sludges. The comparative performance characteristics of dewatered sludge from different dewatering equipment are given in the following tables.

Table 6. The main performance characteristics of sludge dewatering equipment

	Decanter centrifuge	Belt press	Plate filter press
Way of operation	Continuous	Continuous	Batch
Sludge conditioning	Required <sup>(1)</sup>	Required <sup>(1)</sup>	Not required <sup>(2)</sup>
Washing water	Not required	Required <sup>(3)</sup>	Not required <sup>(4)</sup>
Labour	Only supervision	Only supervision	Required during cake discharge
Sensitive to sludge variability	Very sensitive	Very sensitive	Less sensitive
Energy consumption	High	Medium	Low
Maintenance	Sophisticated	Medium	Low

#### Notes:

- (1) Polyelectrolyte (usually cationic): 2-4 g/kg of DS
- (2) Sludge conditioning with inorganic chemicals (Iron salts and lime) is not strictly necessary, but recommendable for enhancing filtration rate and regular performances.
- (3) About 10 m<sup>3</sup>/h of clean water at 4 bars per meter of belt width are required for continuous belt washing.
- (4) Periodical cleaning of filtering clothes is required (minimum once per week).

Table 7. Dry matter content in sludge depending on the process stage and/or type of dewatering equipment

Treatment stage, equipment	DS content %
Sludge after primary clarifier	3 - 5
Thickened mixed primary and secondary sludge (at specific load of about 60 kg DS/m².d	6 - 8
Chamber filter press with chemical conditioning	35 - 45
Belt filter press with use of PE	20 – 25
Centrifuge – decanter	20 - 30
Sludge after stabilization with CaO (mostly after belt filter press or centrifuge)	60 - 90

<sup>\*</sup> Average values for mixed (primary + secondary) tannery sludges.

Sludge drying beds, easily constructed with locally available materials were perceived as optimum solution for tanneries in hot climate developing countries. However, they require a lot of area, the output during rainy seasons drops considerably, there is the problem of malodour, they are not easy to clean and made ready for the next batch etc. For these reasons sludge drying beds are still used mainly by small tanneries not close to residential areas and/or as a short-term back-up for larger units.

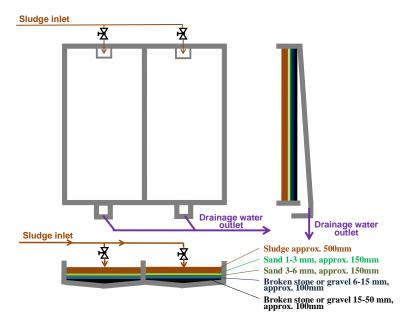


Figure 19. Schematic views of sludge drying beds

The products of the primary treatment are:

- The <u>primary treated effluent</u> (the overflow from the primary settling tank- with only residual amounts of chrome and sulphide and significantly reduced BOD, COD and SS content)
- Dewatered sludge (approx. 40 % DS, its chrome content depending on the type and efficiency of the chrome management system applied).

For the fortunate ones, i.e. tanneries coupled to the sewage system, the on-site treatment often ends here – the biological treatment takes place together with urban wastewaters in large WWW.

Usually, the industrial effluents make only a small fraction of the total volume so that salinity - TDS they bring along does not represent any problem. However, this situation is still rather rare in developing countries.

# 5. BIOLOGICAL (SECONDARY) TREATMENT

The main objective of this phase is to further reduce the amount of organic and other substances still present in the effluent after the primary treatment stage and thereby satisfy the standards/limits for discharge into water recipient. Biologically degradable organic substances are converted to bacterial cells, and the latter are removed from the wastewater.

The biological treatment stage duplicates the processes that take place in nature but under controlled conditions and, especially, at highly accelerated pace; however, the efficiency of this treatment stage largely depends on the biodegradability of the polluting substrate i.e. its inherent capacity to decompose by the biological process. The remaining suspended and colloidal solids are removed by flocculation and adsorption.

While in principle the biological treatment may be <u>aerobic</u>, <u>facultative</u> or <u>anaerobic</u> (or some combination thereof) in practice, almost only aerobic systems are used; exceptionally, in countries with hot climate and where a lot of land is available, facultative (or preferably aerated/facultative) lagoons are also used.

Due to inherent characteristics of tannery effluents, primarily sulphide/sulphate content and related malodour problem, anaerobic treatment is in practice limited to sludge digestion.

Among many variations of the aerobic processes, the most widely used method is (complete mix) the activated sludge treatment with extended aeration; despite some very interesting features, membrane bioreactors (MBRs) have not made significant inroad in the tanning sector.

The activated sludge process can be summarized in the following manner:

Inert matter + organic matter + oxygen +nutrients + microorganisms  $\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$  New microorganisms + CO<sub>2</sub> + H<sub>2</sub>O + additional inert matter

Simply said, the microorganisms are stimulated to convert (eat & digest) harmful, oxygen demanding organic compounds into environmentally more acceptable form (microorganisms) and low energy, stable compounds like water, carbon dioxide and nitrogen gas.

The microbial community that does that job comprises various species of bacteria, fungi, protozoa, sometimes rotifers (multicellular animals only found in very stable activated sludge with long retention times), even nematodes, the composition of the community population depending on a plethora of factors. A typical activated sludge process flow diagram is shown below:

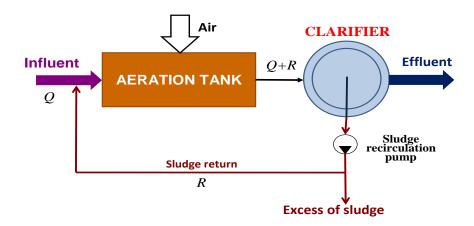


Figure 20. A simplified flow diagram of the activated sludge process

The biological stage is the most complex part of the overall effluent treatment process, with highest share of investment and operational costs, its day-to-day running requiring considerable skills and experience.

#### The main operational parameters

The main operational parameters – expressions important for understanding of the process:

- Total Influent Volume, Q: Volume of the treated effluent [m³/day]
- Tank Volume, V: Aeration tank volume [m<sup>3</sup>]
- Organic Loading, F: The total BOD<sub>5</sub> applied [kg/day]

$$F = (f * Q)/1000$$

where f is the BOD<sub>5</sub> of the influent [mg/l]

• Mixed Liquor Suspended Solids, M:

$$M = (MLSS * V)/1000$$

where MLSS - is the concentration of SS in Mixed Liquor in the aeration tank [mg/l]

Loading factor, F/M:

BOD<sub>5</sub> kg per day per kg of Mixed Liquor Suspended Solids (MLSS) in the aeration tank [mg/l].

Hydraulic retention time, T:

$$T = (V/Q) * 24$$
 where V is the aeration tank volume [m<sup>3</sup>]

Uniform inlet flow distributed over the entire day provides optimum conditions for absorbing the effect of possible peaks of organic load or toxic substances (shock loads) and enhancing the efficiency of the secondary sedimentation. The BOD here is in practice taken to represent the amount of food provided to the microorganisms contained in the system. Hydraulic retention time is actually the average time (in hours) the influent spends passing through the aeration tank (hours); in extended aeration process, typical for tannery effluents it is usually more than 24 hours.

Extended aeration plants are characterized by introduction of wastewater directly into the reactor basin, long aeration, high sludge return ratio, low sludge wastage and high MLSS: the F/M (kg BOD/kg MLSS per day) ratio is only  $\leq 0.05 - 0.1$  in contrast with conventional (0.15-0.4) or high load type (0.4-1.0).

Process	F/M ratio	kgO₂/kg BOD
Extended aeration	0.1	2.0
Conventional	0.3	1.2
High rate	1.0	0.8

The other closely monitored parameters are:

<u>Dissolved Oxygen (DO)</u>, the content of molecular oxygen in the aeration tank (mg/l); extended aeration units are usually operated in such a way as to keep the DO of the mixed liquor at about 2 mg/l.

 $\underline{pH}$ , its optimum normally between 7.0 and 7.5 with an effective process range of 6-9. Reaction between the  $CO_2$  produced from respiration neutralises the excess alkali, adjustment with lime or other needed only if pH drops below 6.

<u>Temperature</u> affects the metabolic and growth rates of the microorganisms responsible. While higher temperature accelerates the growth rate increases it negatively affects the water solubility of oxygen and the oxygen transfer rate.

<u>Nutrients</u>: the nutritional balance of an aerobic system is primarily based upon satisfying the requirements of the cell structure produced by the removal of BOD from waste. Efficient and successful biological oxidation requires a minimal quantity of nitrogen and phosphorus. A BOD: N:P ratio of 100:5:1 in the waste usually insures adequate nutrition. The tannery effluent is very rich in nitrogen and sometimes poor in phosphorus.

<u>Sludge Volume Index (SVI)</u> is the volume occupied by 1 g of activated sludge after settling the aerated mixed liquor in a 1,000 mL graduated cylinder or Imhoff cone for 30 minutes. It provides good indication of sludge compacting characteristics and it is very helpful in determining return sludge pumping requirements.

$$SVI = \frac{Settled \ sludge \ volume \cdot 1000}{Suspended \ solids} \quad \begin{bmatrix} \frac{ml/l}{mg/l} \end{bmatrix}$$

Well settleable and mineralised sludges have SVI < 100.

#### 5.1. Nitrification, denitrification

In order to satisfy the legal limits for nitrogen (ammonia and TKN), very often nitrification and denitrification stages need to be introduced into the biological system. Nitrification requires extensive aeration as well as low F:M ratio (< 0,1) to facilitate conversion of nitrogen containing organic matter into nitrite ( $NO_2$ ) and nitrate ( $NO_3$ ) salts. The crucial role play very specific *Nitrosomonas* and *Nitrobacter* bacteria.

Denitrification is the final step of the conversion where the nitrate is reduced to gaseous nitrogen. It occurs while oxygen levels are depleted and nitrate becomes the primary oxygen source for denitrifying (facultative heterotrophic) bacteria. For the conversion, they need sufficient organic carbon as food, and oxygen which is taken from the oxygen contained in nitrate because there is no other source (thus anoxic conditions must be maintained). In this way nitrate is firstly reduced to nitrous oxide, and then into nitrogen gas which escapes into the atmosphere as gas bubbles during aeration in aerobic tanks. In India, the nitrification and denitrification aspects are not considered seriously especially in CETPs treating effluent from semi-finish to finishing process.

#### 5.2. Aeration devices

Water (effluent) aeration is important business with wide range of models, designs. In addition to cost, reliability etc. the key criterion is the amount of air (oxygen) transfer per KW installed. As mentioned earlier, despite easy maintenance, due to lower transfer efficiency and problems with aerosols and malodour, surface aerators are more and more abandoned in favour submerged turbines, various Venturi type jets and fine bubbles bottom diffusers. Brush rotors are used in oxidation ditches. A few selected aeration systems are shown below:

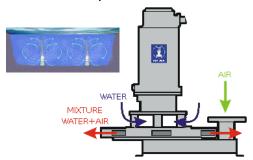


Figure 21. Forced air, submersed turbine aerator



Figure 22. Bottom air diffusers grid with one section and fine bubble dome diffuser

Reportedly, new and more efficient aeration devices such as jet aspirators fixed with mini compressors are being developed and introduced.

# 5.3. Aeration basins, oxidation ditch

Possibly the best system for biological treatment of tannery effluents is the oxidation ditch, a racetrack-shaped aeration basin, with rotary brush or vertical rotors (carrousel) aerators that extend across the width of the ditch as shown in the following figure.

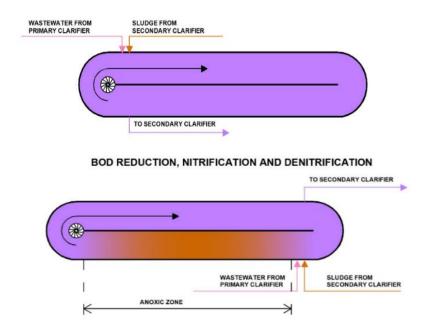


Figure 23. Schematic diagram of oxidation ditches with BOD removal, nitrification and denitrification

In addition to simple construction and easy maintenance, the main advantage of the OD is its resilience to variations in flow, pollution load, including shock loads. It is even possible to combine several ovals and within them maintain different aeration regimes suitable for nitrification and denitrification.



Figure 24. Submersed turbine aerators in the oxidation ditch



Figure 25. View of an oxidation ditch in operation

Owing to the lack of space, many aeration tanks (for example in CETPs in India) are rectangular, with extra depth and appropriate equipment to ensure proper aeration.

# 5.4. Secondary sedimentators

Their design is very similar to those of primary sedimentators, but the operational conditions differ. In addition, the excess – wastage sludge evacuated at the tank bottom is normally bulkier and more difficult to dewater. Important design/performance parameters are:

<u>Surface Hydraulic Loading or Surface Overflow Rate (SOR)</u>: vertical velocity of the influent in the secondary sedimentation tank ( $m^3/m^2$  of tank surface per hour or m/h). SOR of approx. 0.5  $m^3/m^2$  per hour is usually adopted for secondary sedimentation of tannery effluents - i.e. less than for primary clarifiers.

<u>Surface Solid Rate (SSR)</u>: quantity per hour of MLSS (kg) crossing the surface area of the secondary sedimentation tank (kg/ $m^2$  of tank surface per hour) (see primary sedimentation). SSR values between 2.0 and 3.0 kg/ $m^2$  per hour are usually adopted for secondary sedimentation of tannery effluents.

The overflow from the secondary clarifiers represents the fully treated effluent usually fit for discharge into municipal sewer or even the final water recipient – a large lake or a river with adequate flow.

# 5.5. Membrane Bioreactors (MBR)

MBR biological treatment is essentially a version of the conventional activated sludge system with membrane filtering instead of secondary clarifier for solid/liquid separation. Membranes are semi-permeable filters attached to a support matrix, which have a defined pore size. Membranes are operated in a cross-flow modus by pumping a feed solution through the membrane module under pressure and at high velocity. The result is water (permeate) of consistent quality and free of suspended solids. Different configurations of perm-selective membranes can be integrated in the system to achieve micro-, ultra or nanofiltration. The process flow diagrams of conventional and membrane bio-reactor systems are shown below:

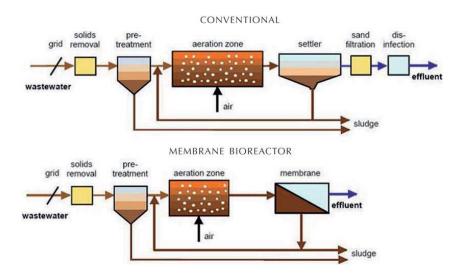


Figure 26. Simplified schemes of the conventional vs. MBR process

This very compact and auto-controlled system can be adopted in a modular way and it produces effluent of high quality. The disadvantages are rather high investment, necessity of nitrification & denitrification, decrease in overall operational capacity of treatment plant due to the fast-declining performance of the membranes and high operational costs depending in particular on membranes working life and energy consumption.

It is argued that over the last decade membranes for effluent treatment have improved and investment as well as operational costs have decreased, making the system a potentially attractive alternative to other biological treatments. The purification efficiency at various stages of treatment are given the following table.

	Physical-chemical		Biological	
Parameter	Reduction %	Approx. value mg/l	Reduction * %	Approx. value mg/l
Suspended Solids (SS)	80 – 90	300 - 600	95 - 98	20-50
Biological Oxygen Demand (BOD₅)	50 – 65	750 - 1500	97- 99	20 – 30
Chemical Oxygen Demand (COD)	50 – 65	1500 - 3000	87 – 93	250 – 400
Total Kjeldahl Nitrogen (TKN)	40 - 50	250 - 300	60 - 70	100 – 200
Chrome	92 – 97	5 - 10	99 – 99.5	< 1
Sulphide	80 - 90	10 - 20	99 – 99.5	< 1
TDS, mainly chlorides and sulphates	No reduction !!			

Table 8. Purification efficiency of the treatment stages referred to raw effluent

# 5.6. Anaerobic biological treatment

As mentioned earlier, despite its higher performance for effluent with high volatile organic content, comparatively lower costs and wide use in some other industries, anaerobic treatment has failed to make any inroad in the tanning industry. The main reason is that the tannery effluent contains high concentration of sulphate, which during anaerobic digestion develops highly toxic, corrosive and flammable hydrogen sulphide gas (H<sub>2</sub>S). This aspect as well as limitations during winter period and other O&M difficulties prevail over other, positive features of anaerobic treatment.

#### 5.7. Other treatment methods

The overall performance and/or specific requirements have limited the use of other treatment methods to some particular situations.

Lagooning may appear a low-cost technology but large land areas far from residential zones are needed and there is a serious problem of sludge accumulation and removal. Trickling filters might be suitable for a smaller unit in a congested area whereas constructed wet-lands (reed beds) are excellent for the final polishing before discharge into the ultimate water recipient but not for full-scale treatment of larger volumes. Depending on the land configuration, cascades can serve a similar purpose.

<sup>\*</sup> Approximately at the load level of 0.30 kg BOD $_5$ /kg MLSS, oxygen requirement of 2.0 kg O $_2$ /kg BOD $_5$  and MLSS 3300 g/m $^3$ 

#### 6. ADVANCED (TERTIARY) TREATMENT

Tertiary and/or advanced wastewater treatment is employed to reduce the residual COD load and/or when specific wastewater constituents are not removed by the previous treatment stages. Drastic reduction of TDS (colloquially salinity) by Reverse Osmosis (RO) supplemented by Multi Effect Evaporation (MEE) also falls into this category.

#### 6.1. Fenton process

The Fenton process is an established and very effective oxidation process widely adopted in industrialized countries which reduces residual pollution by chemically oxidizing recalcitrant COD i.e. the matter that remains after the biological treatment because the microorganisms did not find it digestible.

The Fenton treatment is based on the formation of hydroxyl radicals that have a strong oxidation capacity and can fully oxidize refractory organic pollutants. These powerful free radicals are generated by the hydrogen peroxide  $(H_2O_2)$  in the presence of suitable catalyst, usually the ferrous sulphate  $(FeSO_4)$ . The stages of Fenton process are given below:

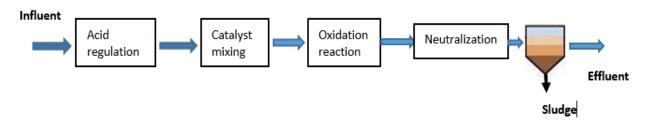


Figure 27. Stages of the Fenton process

Though the Fenton process is an efficient tertiary treatment in reducing non-degradable COD, it requires close monitoring with skilled man power. The generation of additional sludge and high O&M cost are other limitations.

# 6.2 Ozone Treatment

Advanced oxidation treatment using ozone is being adopted in some of the CETPs to reduce the non-degradable COD and for colour removal. This process has high capital cost and energy requirements.

#### 7. SLUDGE DISPOSAL

It is important to realize that in addition to purified effluent, ETPs and CETPs also produce large volumes of sludge that has to be dealt with: ideally reutilized or disposed of in safe and environmentally acceptable manner.

In comparison with sludges from domestic wastewater treatment plants, the sludge from tannery effluent treatment plants has higher inorganic matter and higher heavy metal content, and, especially, higher chromium and sulphur compound content. However, the main stumbling block is the chromium content, the pertaining legislation and practice in various countries differing a lot.

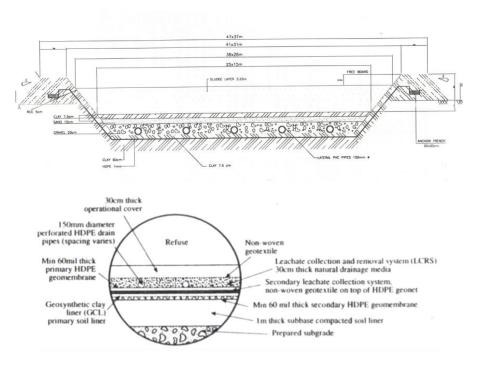
In any case, handling, dewatering, storage and transport of sludge and solid wastes from ETPs & CETPs should also be safe and not contaminate the surrounding; thus, for example, the collection points should be protected against weather (e.g. rain).

Untanned and tanned wastes generated by the tanning industry are not classified as hazardous waste in industrialized or developing countries. In future European legislation will prohibit the disposal in landfills of solid waste containing more than 10% organic matter. Currently, the permissible limit in India is 20% organic matter for the disposal of dewatered sludge in secured landfills (SLF). This limit is likely to be reduced in the future.

Chromium content in tannery sludge is the main constraint on its use or safe disposal. Given the high toxicity of hexavalent chromium, many environmental standards also limit total chromium. This limitation arises for want of insufficient knowledge of the difference in properties between trivalent and hexavalent chromium or for fear that trivalent chromium may be transformed into hexavalent chromium during waste disposal/re-use or chlorination of drinking water.

Landfilling in ordinary or special landfills remains the prevailing disposal method. Regrettably, in many developing countries, properly designed, constructed and/or maintained landfills are not available; tannery sludge is just dumped without proper control.

Other, more advanced sludge handling and disposal methods are chemical conditioning with quick lime, thus increasing the sludge dry solids content and improving its appearance and smell, composting (usually aerobic, in either open or closed systems, the compost applied in cultivation of inedible plants) and thermal treatment (drying, vitrification, pyrolysis—gasification etc.) resulting in lightweight aggregates/oil. The decentralized secured landfill system has been developed and adopted in India and other Asian countries. The typical cross section of SLF systems, bottom layers, laying of HDPE sheet, side walls, etc., are shown in the following figures.



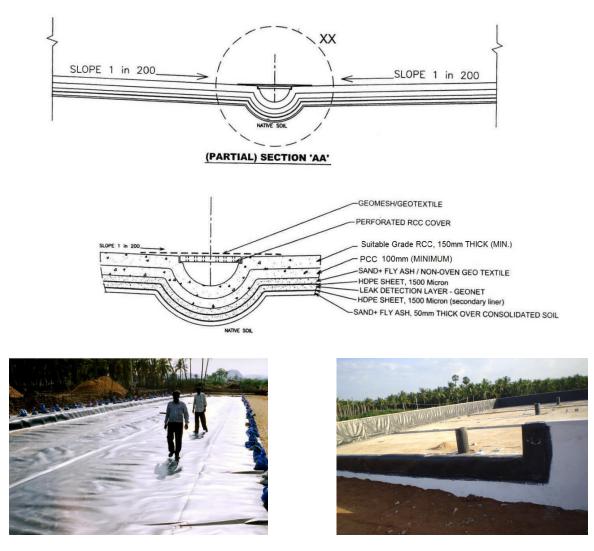


Figure 28. Landfill: Cross section, bottom layers & laying of the HDPE sheet

Source: S. Rajamani

It is important to have a leachate collection arrangement, the leachate to be sent for treatment or, where applicable, to be sprinkled over the top of the landfill.

Sludge from tannery effluent treatment plants is not treated as hazardous material in industrialized countries. However, the presence of chromium beyond prescribed levels limits its alternative uses and hence landfill is the preferred mode of disposal. With stricter regulations governing the disposal of sludge with an organic content of more than 10% or with a potential for value recovery, including the recovery of energy, sludge disposal costs in industrialized countries are expected to rise further. Regulations in this regard in developing countries, although strict (many countries treat sludge as a hazardous substance), are rarely enforced. In India, CETPs generally dispose of sludge on their own premises. Alternative utilization options attempted in India have not yet resulted in a popular mode of disposal. Accordingly, sludge disposal costs in Europe are significantly higher than in India.

As per the regulations of the Government of India, sludge that contains less than 5,000 mg/kg of total chromium and less than 50 mg/kg of hexavalent chromium is not considered hazardous. However, all category of tannery sludge is expected to be disposed in the Secured Land Fill (SLF) irrespective of the concentration of chromium in the dewatered sludge.

#### 8. COMMON EFFLUENT TREATMENT PLANTS (CETPs)

This approach was originally adopted in Italy to tackle the problem of polluting wastewaters emanating from individual, highly specialized leather making units in large agglomerations, the system that is also well suited for the situation in many developing countries. Traditional, often family owned tanning units lacked not only the necessary investment potential and specific technical skills but also the space needed for installing the treatment facilities; CETPs servicing entire tannery clusters were set up from 1995 onwards in Türkiye, across Asia, in China, India, Pakistan, Bangladesh etc.

This concept was then followed in relocations and/or establishing new leather centres/clusters; for practical reasons (only gradual increase in volumes of effluents, seasonal fluctuations), new CETPs have been designed in modular way.

Estimating effluent volume is one of the most challenging tasks in planning and designing CETPs mainly due to large oscillations in availability of raw hides and skins and market demand. Seasonal peaks associated with religious festivals are also very pronounced in developing countries. Modular approach to some extent helps coping with this challenge.

An important aspect of CETPs operations is the effluent collection network, very often a combination of pressure and gravity line. Scale forming in gravity lines, silting and generation of toxic fumes  $(H_2S)$ , especially in deep manholes, are the major issues in operation and maintenance of effluent collection and conveyance pipelines. Many countries, including India, started enforcing the TDS parameter in the discharge standards. The safe disposal / utilization of the hazardous category, chrome containing sludge from the CETPs and non-degradable solid wastes from tanneries such as chrome shavings are the major challenges yet to be fully resolved in many Asian countries.

#### 9. REVERSE OSMOSIS (RO), ZERO LIQUID DISCHARGE (ZLD) CONCEPT

This concept has been largely implemented in several traditional tannery clusters in the very arid areas in the state of Tamil Nadu, India where dramatic situation with water and soil pollution along the Palar River together with public and buyers' pressure eventually prompted the state environmental authorities to enforce the discharge limit for Dissolved Solids (inorganic) of 2100mg/L.

The fully-fledged physical-chemical and biological treatment is followed by tertiary treatment units such as Dual Media Filters, Microfilters, Ultrafiltration (UF), two or three stage Reverse Osmosis (RO) and evaporation of RO rejects of volume using Multi Effect Evaporator (MEE) and Agitated Thin Film Dryer (ATFD).

Essentially, the ZLD systems concentrate dissolved solids present in the fully treated effluent by RO and MEE/ATFD until only damp residual remains. Nearly all purified water, the permeate (about 80%) and condensate (close to 20 %), is reclaimed and supposedly reused. Reportedly, there are some difficulties in the reuse of condensate due to malodour caused by the presence of ammonia.

The ZLD is actually not so much treatment but rather a salt sequestration and removal system. Due to its complexity, it requires close and continuous monitoring of many parameters. The schematic diagram on the principle of RO system is shown below.

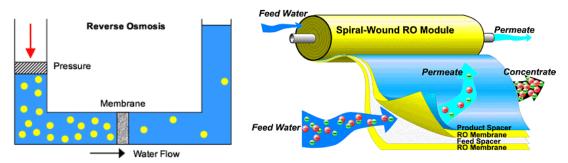


Figure 29. Reverse osmosis (RO): principle, schematic diagram

Preparatory, post-CETP "conditioning" steps, in particular water softening, often require dosing of different chemicals, including salts, which is quite a paradox for what is essentially a salt removal system. The Ultrafiltration (UF) system prior to RO system installed in one of the tannery CETP in India is shown below:



Figure 30. Ultrafiltration (UF), an important step in preparation for RO

Source: S. Rajamani

During initial years of operations, the estimated yearly average water recovery (permeate) rate for three CETPs with RO+MEE system was about 72 - 76 %. However, the consumption and the cost of energy exploded. The salt residue produced and by now accumulated in terms of thousands of tons poses a very serious environmental challenge. Since it is a mixture of mainly chlorides and sulphates and there is no viable technology for their separation, the challenge is to find a way for its utilization and/or safe disposal.

There is no doubt that industrial scale ZLD in treatment of tannery effluents is technically feasible. However, due to very high capital and operation costs (in particular power consumption),

including the problem of storage and disposal of solid residue its wider acceptance is quite unlikely. A possible viable option might be separate evaporation of only highly concentrated saline streams (soak, pickling) preferably without RO because that requires another, smaller volume but parallel full-scale treatment.

Potential alternatives for survival of the local tanning industry include a combination of shortand long-term options such as construction of proper sewage systems in large townships facilitating mixing and joint treatment of tannery and municipal waste water, slaughter of some livestock (buffaloes, goats/sheep) and salt-free preservation, concentration of wet blueing etc.

# 10. OCCUPATIONAL SAFETY AND HEALTH (OSH) AT (C)ETPS

#### 10.1. General

The management should specify and provide appropriate Personal Protective Equipment (PPE) such as boots, gloves, goggles, face shields etc. for tasks where it is required. Similarly, safety (warning, mandatory) signs need to explained and suitably displayed.

The entire effluent treatment area tends to be slippery, both metal and concrete surfaces. Employees working over or near water tanks where there is a risk of drowning should be provided with approved life jackets or buoyant work vest; ring buoys with lines should also be readily available as shown in the following figure.



Figure 31. A ring buoy conveniently positioned at the treatment plant

#### 10.2. Risks associated with the hydrogen sulphide (H<sub>2</sub>S), malodour problems

Odours associated with wastewater are difficult to quantify because they are caused by a wide variety of compounds, it is a nuisance that is more qualitative than quantitative: sensitive persons easily detect very low concentration of odoriferous substances in the air (sulphides/other sulphur compounds, ammonia, amines, etc.). Local geographic and climatic conditions such as wind direction, land shape, air humidity, ground and air temperature, etc. Along the treatment line the main sources of bad smell are:

- Oxidation of sulphide in the beamhouse streams
- Equalisation, homogenization
- Sludge thickening
- Biological aeration
- In-plant storage of the dewatered sludge
- (Temporary) sludge disposal site

Yet, the main source of bad smell remains stripping of hydrogen sulphide; however, it is not the concentration of sulphide *per se* but lowering of pH: the not disassociated  $H_2S$  is present only at pH below 10. Thus, it is crucial to control pH and in case of need alkalis like NaOH or lime to make pH > 9.5-10 are added. More extensive, uninterrupted aeration may help but sometimes rigorous (and expensive) methods like adding hydrogen peroxide or pure oxygen are necessary. Nowadays, in some places, nearly the entire ETP is covered and the exhaust air purified.

Despite the fact that outdoor the risk of H<sub>2</sub>S is lower, the area should be monitored using fixed, portable and personal detectors, and all concerned workers should be well equipped and trained to deal with emergency situations.

The tanning industry is not a major air polluter. The main air pollutants are hydrogen sulphide and ammonia emanating from liming, deliming and pickling operations and waste treatment operations as well as volatile organic compounds (VOC) used in the finishing department. This holds especially true for tanneries with poor housekeeping practices, including improper handling of solid waste. Incineration of tanned leather wastes is a health hazard whereas the new sludge treatment technologies (such as thermal drying and pyrolysis) may produce exhaust gases (fumes) that pose a threat to the environment and workforce alike. Standards governing exhaust gases have been set and are relatively strictly enforced in industrialized countries.

#### 10.3. Noise

The main source of noise are air blowers supplying compressed air to aeration systems; they need to be appropriately positioned and dampened. Pumps, screening devices and sludge dewatering equipment can also be rather noisy.

# 11. MONITORING, TREATMENT COSTS

The extent of monitoring activities largely depends on local legal requirements and (C)ETP size and it includes a wide range of parameters: effluent volume(s), peak loads, pollution loads before and after treatment, chemicals dosing, dissolved oxygen (DO), sludge volume index (SVI), DS content in sludge etc. as one aspect of the overall company's Environmental Management System (EMS). The costs of treatment vary a lot, primarily depending on the local costs of power, chemicals, sludge utilization and disposal options, finances and labour as shown in the following figure.

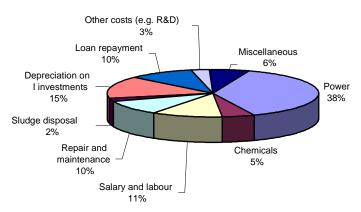


Figure 32. Typical structure of treatment costs in selected CETPs in India (before ZLD)

The highest component: power; sludge handling and disposal costs comparatively low. However, if the reverse osmosis (RO) and evaporation (MEE) stages are installed, the cost of energy escalates even further.

In industrialized countries the largest component, often around 40 % of the total costs, is dewatering and safe disposal of solids (sludge).

While working out the costs of an ETP in an individual tannery is quite straightforward, different methods are applied to compute the distribution of the CETP operation costs among individual tanneries. The key parameters used are typically the following:

- Water consumption, m³/day
- Production capacity, tonnes of wet salted hides/day
- Actual pollution load in terms of COD (even better COD removed), suspended solids, TDS, sulphide and chromium
- Production output, m<sup>2</sup>/day of wet blue, crust or finished leather

Pollution load-based distribution of costs requires appropriate on-/off-line monitoring.

A typical flow chart of a full-fledged tannery effluent treatment plant is shown in the following figure.

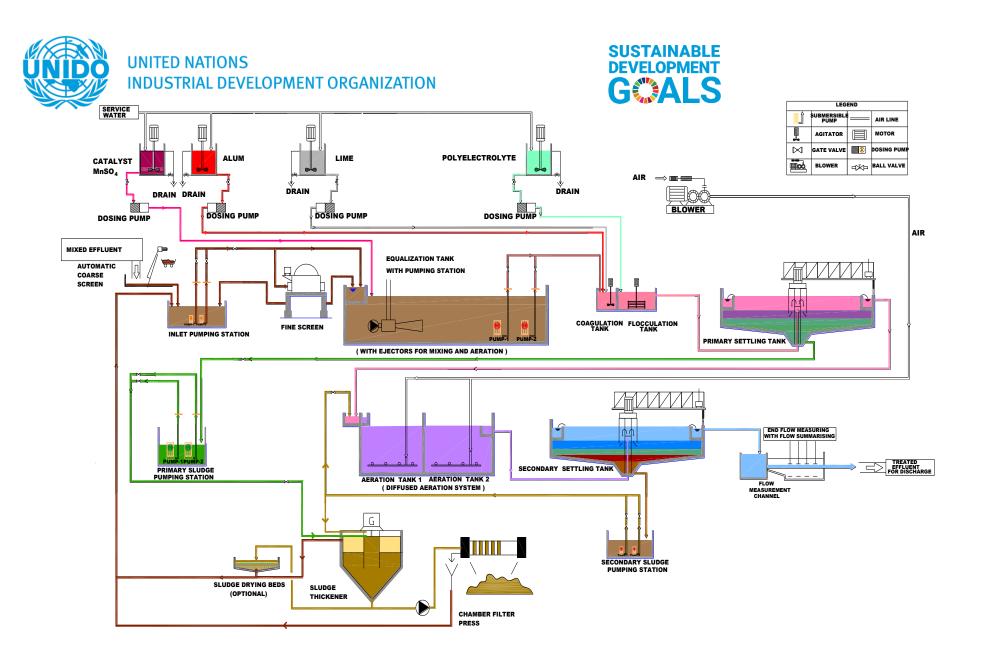


Figure 33. Simplified flow-chart of the fully-fledged tannery effluent treatment plant

#### 12. CHALLENGES AND OPPORTUNITIES

The following are the main immediate and long-term challenges to the tanning industry.

# 12.1. Science & technology

- Avoidance of salt preservation, reduction in salt usage in the process
- Replacement of currently used non-degradable / and hazardous chemicals with more environment friendly chemicals
- Significant improvement of efficiency and exhaustion of chemicals used in the process
- Utilisation of non-collagen, i.e. non-leather making substances and solid waste in general
- Recycling of residual chemicals, leather and leather products

# 12.2. Global pressures & public perception of leather under influence of misinformed groups and lobbies

There is a lot of incorrect and obsolete information in public media linking the leather industry with cruelty toward animals, deforestation (in particular rain forests) and even to greenhouse gases (GHG), especially methane generated by livestock. A few remaining ugly spots in developing countries are presented as representative of the whole industry; some of them in North Africa, in terms of production are irrelevant and actually mainly kept as tourist attractions.

The fact that tanners all over the world use only "instant" powders containing harmless trivalent chromium (Cr³+) salts is disregarded and chrome tanned leather and leather goods made of it are drummed as being carcinogenic due to presence of hexavalent (Cr<sup>6+</sup>) and, in the best case, only chrome-free leathers should be used. Paradoxically, even fossil based synthetic materials are sometime preferred over leather.

Admittedly, it (unnecessarily) took some time for tanners to realize and to accept that under some circumstances (long storage, high temperatures, use of low quality fatliquors etc.) small amounts of  $Cr^{3+}$  can be oxidised to  $Cr^{6+}$  form. Again, the real risk from the  $Cr^{6+}$  is regularly grossly exaggerated. Furthermore, nowadays this can be easily prevented by using appropriate retanning agents (e.g. tara vegetable tannin) and appropriate fatliquors.

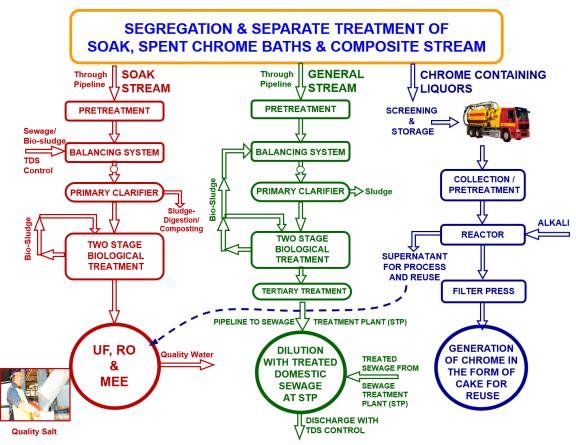
Actually, it is astonishing that it is too often overlooked that tanners convert a waste product from the meat industry into a highly versatile, sophisticated and yet beautiful material. And the cell cultivated leather appears to be still pretty far from replicating the fascinating natural structure.

Due to their (in old days) noxious nature, tanning activities and tanners in virtually all cultures all over the globe were assigned to a very low social status, very often entirely outside "normal" society. In the worst-case scenario, such deeply rooted biases compounded by very

aggressive campaigns based on false claims and agendas and possibly excessive legislation might jeopardize the future of the tanning industry as we know it.

# 12.3. Total Dissolved Solids (TDS) and salinity

Crystal clear, odourless water resulting from a full-fledged conventional treatment is in arid regions not only useless but actually potentially harmful due to TDS content (colloquially salinity). This is compounded by the fact that currently only a few developing countries have large meat processing plants offering the possibility of skipping the preservation step (salting) and almost immediately proceeding with tanning up to wet blue or even fully finished stage. A new concept of segregation, separate treatment of soak, spent chrome baths & composite streams is shown in the following process flow diagram.



<sup>\*</sup> Note purification & treatment of the supernatant from the central chrome recovery Source: S. Rajamani

Figure 34. One proposal for segregation & separate treatment of soak, spent chrome baths & composite streams

Attempts with mechanical desalting of hides and skins as well as solar evaporation pans (including accelerated evaporation trials) proved to be of little impact.

More recently, a system where treated general effluent joins municipal wastewater, spent chrome floats are collected from the entire cluster and chrome recovered at the central plant whereas Reverse Osmosis (RO) and Multi Effect Evaporation (MEE) are limited to the soak stream has been proposed.

Traditionally, tanning activities have been associated with the proximity of water. Nowadays, due to TDS issue, the proximity of large urban agglomeration with proper sewage and wastewater treatment plants is additional precondition for survival of tanneries in arid regions. Furthermore, existence of large abattoirs might eventually increase the scope for processing fresh hides and skins. At the same time, relocation of tanning capacities, even if limited to wet processing stage, has its its serious social consequences.

## 12.4. Safe disposal of (chrome containing) sludges

A number of solution for utilization and/or safe disposal have been proposed, practiced, tested, applied at pilot and industrial scale: landfill, land-application, land-reclamation, composting, anaerobic digestion, thermal treatment, vitrification, pyrolysis, brick making etc., none of them quite satisfactory. There is certainly no universal solution for sludge utilization/application. Each (C)ETP produces sludge of specific characteristics and various regions and countries have quite different regulation for sludge utilization. Therefore, prior to any (C)ETP construction detailed assessment of options should be prepared and the most suitable application proposed.

#### 13. CONCLUSIONS

The cattle, sheep and goats are reared for their value in dairy products, wool and for their meat, never bred and raised for their skins.

It is very unlikely that the majority of the world population will turn vegetarian and there are no signs of dramatic increase of utilization of raw hides and skins for non-tanning purposes. Thus, the meat industry will continue providing the basic raw material to the leather industry that transforms the natural inter-woven structure into a variety of leather types suitable for very different uses: footwear and apparel manufacture, car industry, equestrian sports etc.

The leather industry needs to continue its efforts in improving its performance, from water consumption & effluent treatment, exhaustion of chemicals, utilization of solid waste and sludges, energy management, adherence to high Occupational Safery and Health (OSH) standards to implementation of Corporate Social Responsibility (CSR) policies both at the national and global level.

Similarly, it is important to take a proactive role in battling negative publicity and spreading of misleading information by fake green lobbies and pressure groups. Better coordination among various national, regional and global leather organizations, including R & D institutions would make a stronger impact. Continued interaction with the leather industry clusters and dissemination of technology by the national and international institutions are essential.

The expanding leather products sector (footwear, leather goods, apparel), including significant local consumption, points towards competitive and successful overall leather industry in developing countries.

The scope for utilization, possibly even recycling of disposed leather products (apparel, footwear, leather goods, furniture and transport upholstery) might turn vital for the long-term perspective of the entire leather sector. A paradox here is that fashion changes

contribute to higher demand but at also the volume of disposed leather items; finally, its longevity is another proof in favour of leather's sustainability.

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