



Pollutants in tannery effluents

Sources, description, environmental impact



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This training material is primarily intended to meet the needs of tanners and people of different profiles associated with environmental protection in the leather industry in developing countries.

The information and data contained therein are drawn from a number of UNIDO studies and field reports and authors’ own experience. Sources such as IULTCS/IUE and EU BREF document are gratefully acknowledged.

Open sources, including manufacturers’ promotional materials placed on web have also been used to compare and/or supplement the existing information.

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Foreword

Confronted with increasing legal and social pressures, no tanner can afford the luxury of not being familiar with the main issues and principles of environmental protection pertaining to tannery operations.

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

The effect of excessive pollutant levels commonly found in tannery effluents can be severe; their impact is here described for general guidance. The main problems presented by those components are summarised together with an outline of the methods used by authorities to determine the levels of those components in effluent.

The lessons that follow are to help tanners and tannery managers to acquaint themselves with the main pollutants, their impact on environment and the basic principles and prevailing methods of tannery effluent treatment. This knowledge should also make them better equipped for a dialogue with the factory's own environmental unit, waste water treatment specialists as well as with environmental authorities and NGOs.

Systems such anaerobic treatment, lagooning or constructed wet lands - reeds, which, despite some interesting features failed to gain wider acceptance are not included.

In order to keep it short and concise, there are many simplifications and omissions of details; therefore, for an in-depth understanding of the complexities of dealing with effluents and solid wastes (sludge) it is recommended to consult the extensive literature on this subject.

Pollutants discharge norms

In principle, limits for different pollutants in effluent are defined in two ways:

- Based on standards which are widely applied and found generally acceptable (i.e. tends to ignore specific individual situations).
- Based on mass-balance of key pollutants, i.e. the quality of the recipient water after receiving and mixing with the effluent; here the scale of dilution in the actual recipient, including its capability to cope with pollution emanating from other sources is also taken into account.

Table 1 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.
COD	180	1800 kg
BOD ₅	90	900 kg
Suspended solids, SS	120	1200 kg
Cr ³⁺	5	50 kg
S ²⁻	5	50 kg
Total Nitrogen, TKN	14	140 kg
Cl ⁻	180	1800 kg
(SO ₄) ²⁻	80	800 kg
Oil and grease	10	100 kg
TDS *	400	4000 kg
pH	6 - 9	

* The main constituents of the TDS are chlorides (Cl⁻) and sulphates (SO₄²⁻)

In practice, most cases legislative authorities define the quality of (treated) effluents depending on the type of recipient: river, lake, sea. Some norms specify the permitted quantity of impurities to be discharged into the recipient per day, whereas in some cases limits are linked to the total amount of waste water discharged. Also, in some cases only a few parameters are subject to control while in others more than two hundred are prescribed.

Table 2 Typical pollution load, conventional leather technology, concentrations in composite effluent; water consumption/discharge 25 m³ water/tonne of wet salted hides

Parameter	Pollution load kg/t of w.s. hide	Concentrations in composite effluent at 25 m ³ of water/t of w. s. hides	
		Unit	Values
COD	180	mg O ₂ /l	7200
BOD ₅	90	mg O ₂ /l	3600
Suspended solids, SS	120	mg/l	4800
Cr ³⁺	5	mg Cr/l	200
S ²⁻	5	mg S/l	200
Total Nitrogen (TKN)	14	mg N/l	560
Cl ⁻	180	mg Cl/l	7200
SO ₄ ²⁻	80	mg SO ₄ /l	3200
Oil and grease	10	mg/l	400
TDS	400	mg/l	16000
pH		6 - 9	

Standards within one and the same country can vary from one region to another. Typically, the central authority stipulates minima and local authorities can insist on even higher levels of purification. Sometimes tannery effluents are not subject to specific limits; they are covered by overall legislation pertaining to the discharge of industrial waste.

In industrialized countries tannery effluents are normally discharged into sewage systems (indirect discharge) and treated together with urban waste waters in municipal waste water works before being returned to the environment via surface waters.

Table 3 Typical pollution load, conventional leather technology, concentrations in composite effluent; typical discharge limits for surface waters

Parameter	Unit	Average total pollution load	Typical limits, surface waters
COD	mg O ₂ /l	7200	125 – 250
BOD ₅	mg O ₂ /l	3600	30 – 40
Suspended solids, SS	mg/l	4800	35 – 100
Cr ³⁺	mg Cr/l	200	1.5 – 2.0
S ²⁻	mg S/l	200	1.0 – 2.0
Total Nitrogen (TKN)	mg N/l	560	Locally specific
Cl ⁻	mg Cl/l	7200	Locally specific
SO ₄ ²⁻	mg SO ₄ /l	3200	Locally specific
Oil and grease	mg/l	400	Locally specific
TDS	mg/l	16000	Locally specific
pH		6 - 9	5.5 – 9.5

Table 4 Performance of one European Common effluent treatment plant, CETP Tannery and municipal waste water

Parameter mg/L	Average composition of tannery effluent received in 2009	Composition of treated blend of tannery and municipal effluent before discharge
Tanneries	160	
Volume	30,000 m ³	30,000 m ³ + 8-10,000 m ³ municipal
pH	7.9	
COD	5551 mg/L	101 mg/L
BOD	2246 mg/L	< 5 mg/L
TKN	430 mg/L	6 mg/L
TSS	2263 mg/L	10 mg/L
Cl ⁻	2344 mg/L	1485 mg/L
SO ₄ ²⁻	1542 mg/L	1328 mg/L
Cr ³⁺	78 mg/L	0.26 mg/L
S ²⁻	70 mg/L	Not detectable

The level of purification of mixed tannery and municipal waste water shown in the table above is outstanding and considerably better than achieved in a typical tannery effluent treatment plant.

Sampling and laboratory analysis

The composition of an effluent sample and thus the results of laboratory analysis are dependent upon the sampling technique which, ultimately, can have a bearing upon the apparent performance of a tannery against set limits.

Two main sampling methods are acceptable.

- Composite: samples taken over a 24 hour period and mixed together.
- Spot (grab) samples: a single sample is taken for analysis.

Ideally, composite samples should be taken by automatic sampler, with 24 samples being taken at hourly intervals and mixed before analysis. As a rule, environmental authorities take samples of mixed, treated effluents before discharge into the final recipient but sometimes samples of individual streams within the tannery compound are also taken. In any case, to reduce variables, the sampling point should always be the same.

The position of the sampling head is decisive. If it is too low, sludge might be drawn into the sampler. This is also an important factor when spot samples are taken, since they are often taken manually.

When samples are taken by an authority such as EPA, a duplicate sample should be retained by the tannery. The sample should be shaken before the duplicate is poured; the sample bottle should be clean, filled to the brim, airtight and kept under cold conditions for a second round of analysis if there are reasons for doubt.

Laboratory analysis

Laboratory analysis of all pollutants follows very detailed, specific procedures requiring particular training and practical experience. Within this course, in the chapter **Main pollutants – Description and general impact**, only tentative outlines for analysis of individual pollutants are provided for general information and understanding. For greater accuracy and conformity of analysis consult the latest edition of the **Standard Methods for the Examination of Water and Wastewater**, prepared and published jointly by: **American Public Health Association, American Water Works Association and Water Environment Federation**. Practical suggestions relating to the range of parameters to be monitored, the frequency of analysis and the laboratory facilities required are to be found in the UNIDO paper entitled **Selection of Equipment for Laboratories Monitoring Pollution in the Tanning Industry, Manual on Laboratory Equipment and Reagents** (UNIDO document number V.94-24950 6955E, 12 July 1994, English, French, Spanish and Chinese).

Laboratory analysis are being continuously improved, better (faster and/or more accurate) methods introduced, some of them tuned to meet specific individual requirements.

Gross solids

Gross solids typically are large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags; they can cause very serious problems such as blockages in inaccessible pipe work, burned out pump motors or broken rotors. If discharged into gullies, ditches or water courses the debris settles out very rapidly leading to stagnation or even flow blockages.

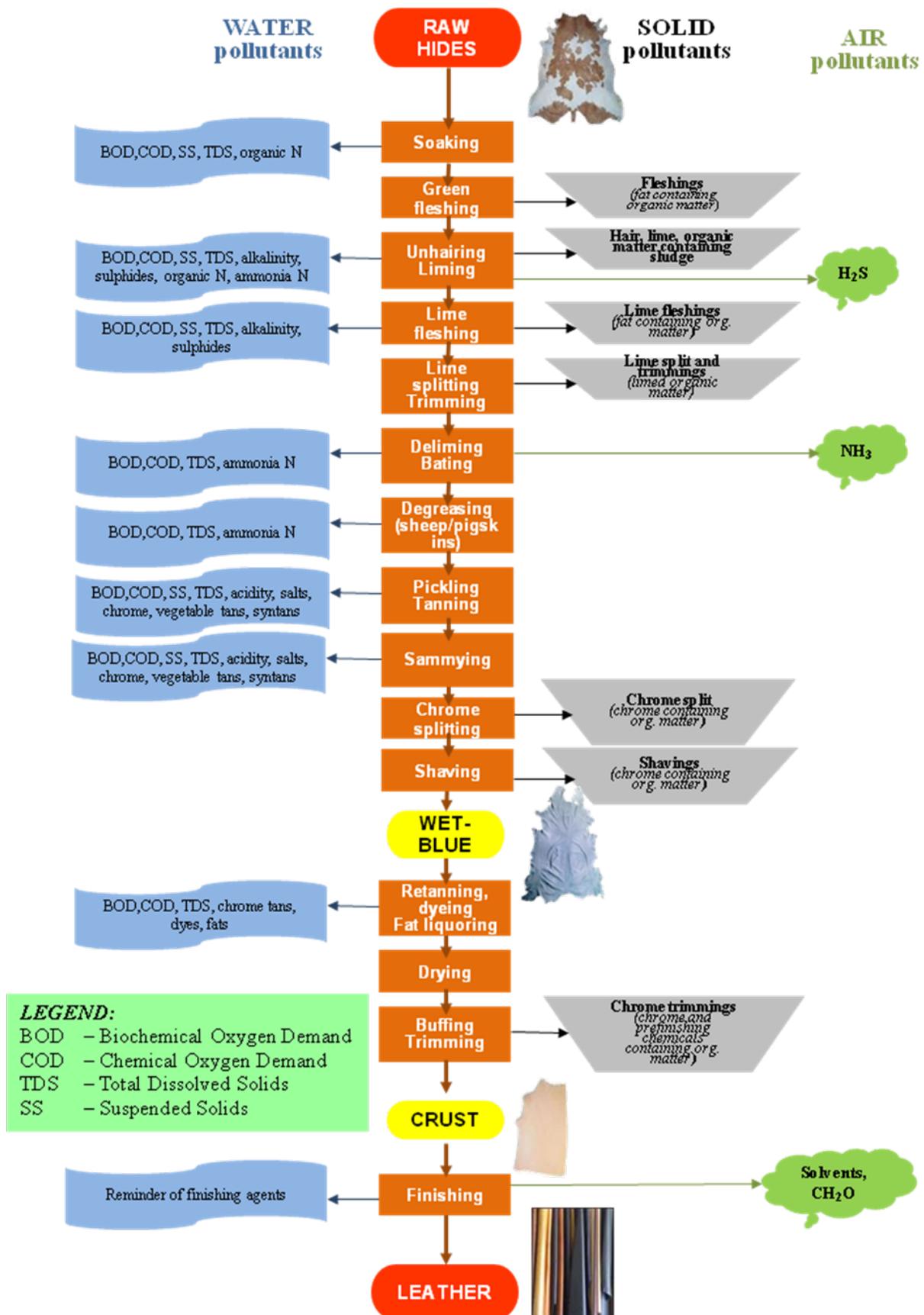
Gross solids can be easily removed by means of coarse bar screens set in the waste water flow.

Gross solids are larger than a sampling machine can handle, hence they are not measured and are not subject of usual effluent analysis.

Figure 1. Typical bar screen



Sources and types of pollutants generated in leather processing



The table below shows the contribution by the main processing stages to the total pollution load.

Table 5 Typical pollution load
Conventional technology, contribution from various process stages, %

Parameter	Total load kg/t of wet salted hide	Contribution to effluent total load, %			
		Beamhouse	Tanyard	Post-tanning	Finishing
COD	180	70 - 80	5 - 10	10 - 15	0 - 5
BOD ₅	90	70 - 80	6 - 8	8 - 15	0 - 5
SS	120	77 - 82	5 - 7	10 - 12	0 - 3
Cr ³⁺	5	-	67 - 71	29 - 33	-
S ²⁻	5	100	-	-	-
TKN	14	82 - 90	0 - 6	10 - 12	-
Cl ⁻	180	68 - 83	14 - 27	3 - 5	-
SO ₄ ²⁻	80	11 - 18	45 - 67	22 - 36	-
TDS	400	58 - 66	20 - 23	13 - 20	-

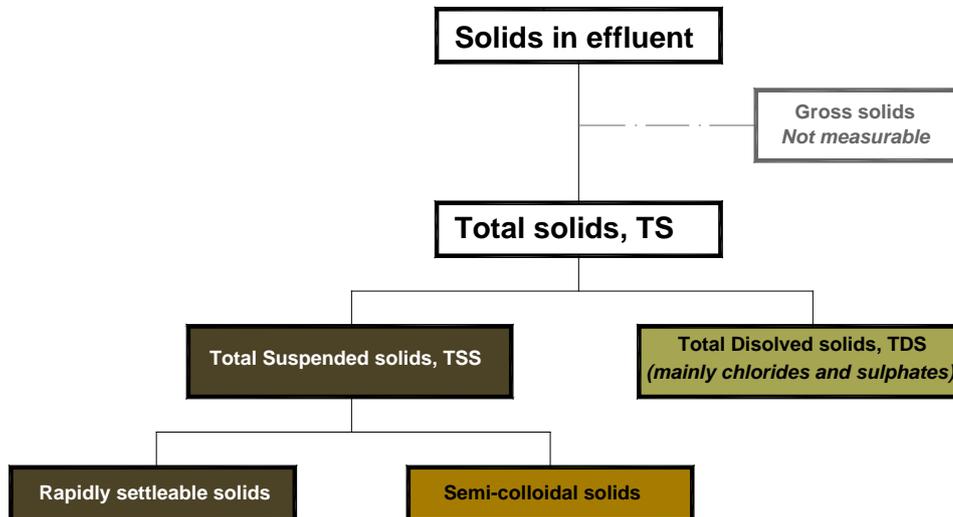
The main components of TDS are chlorides and sulphates.

Beamhouse is by far the largest contributor, typically 70 – 80 % of the overall pollution load; the major part of sulphates comes from tanyard and post-tanning, whereas chrome emanates from tanyard and post-tanning only i.e. from main tanning and (chrome) retanning, including from “bleeding” from sammying. Thus, the main targets of pollution prevention – cleaner technologies are the beamhouse and tanyard.

In recent times, noise, perceived as another important pollutant, is receiving more attention. While its intensity in decibels, dB (unit of measurement used for sound levels) varies, noise is present in virtually all stages of leather manufacture; this issue is, however, usually addressed within the context of the Occupational Safety and Health at work (OSH).

Total solids, TS

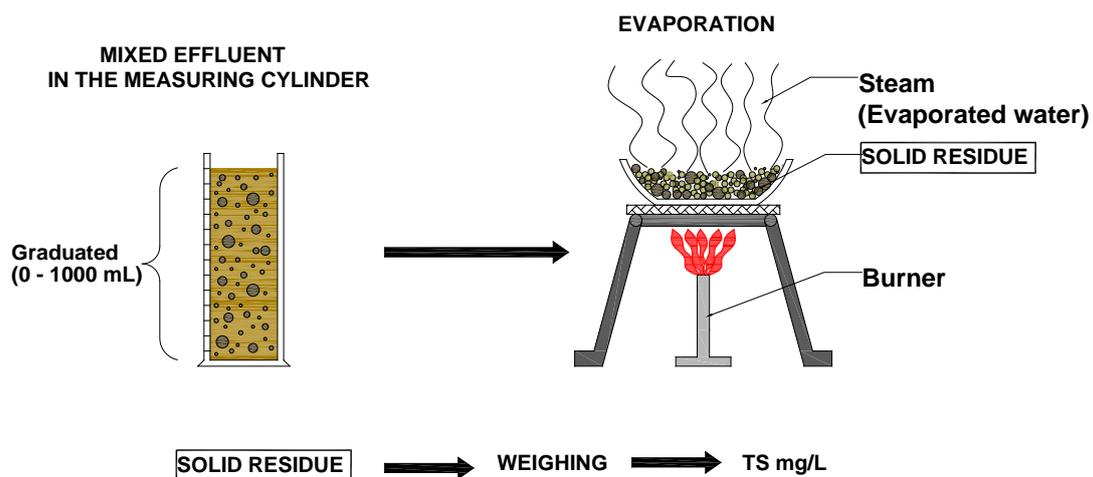
Total solids, TS are made up of all measurable solids present in the effluent. They consist of two components i.e. of dissolved solids (**Total Dissolved Solids, TDS**) and of insoluble, suspended (**Total Suspended Solids, TSS**). The Total Suspended Solids, TSS, in turn largely consist of (rapidly) settleable solids although semi-colloidal solids cannot be quite ignored.



The quantity of Total Solids, TS is determined by weighing the amount of solid residue left after evaporation of a known volume of mixed raw effluent and it is expressed in mg/L.

Description and environmental impact of each type of solids is given separately.

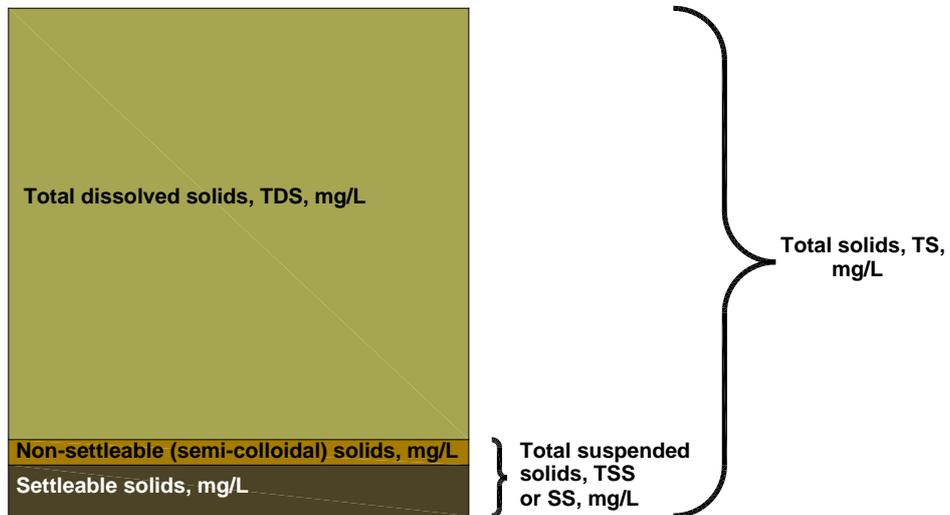
TOTAL SOLIDS



In a typical tannery effluent the largest component among solids are Total Dissolved Solids, TDS.

SOLIDS BALANCE IN THE TANNERY WASTEWATER

Approximate scale



Characteristics and the environmental impact are given for each category of solids separately.

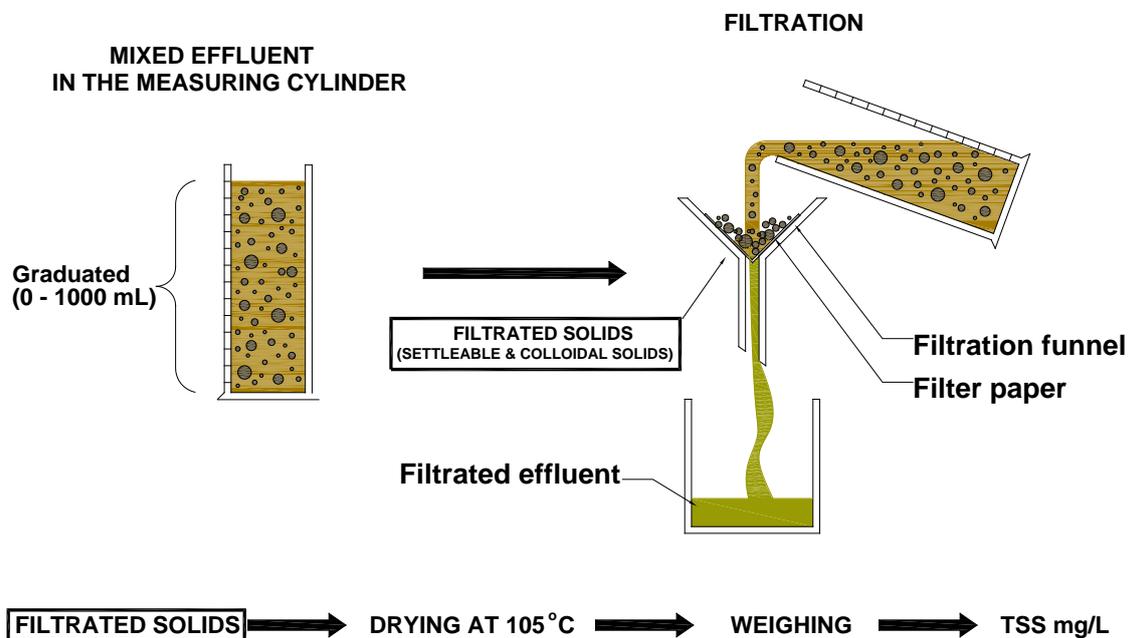
Total Suspended Solids, TSS

Total Suspended Solids, TSS are made up of solids of two distinct characteristics:

- Solids with a rapid settling rate (settleable solids)
- Semi-colloidal solids

To measure the Total Suspended Solids, TSS, i.e. both settleable and semi-colloidal solids, a known volume of effluent is taken and filtered through a filter paper which is then dried and re-weighed. The difference between this weight and that of the original paper is the weight of the dry solid material contained in the sample.

TOTAL SUSPENDED SOLIDS



Substances present in the TSS significantly contribute to the biochemical and chemical oxygen demand (BOD & COD) and thus to the overall pollution load. Also, suspended solids are mainly responsible for the amount of sludge generated in the course of effluent treatment.

The globally prevailing discharge limits for surface waters for Suspended Solids are within the 35 – 100 mg/L range.

Settleable solids (Solids with a rapid settling rate)

Settleable solids comprise material that can be seen in suspension when an effluent sample is shaken, but settles when the sample is left to stand. The majority of these solids settle within 5-10 minutes, some fine solids require more than an hour.

Settleable solids originate from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beamhouse processes.

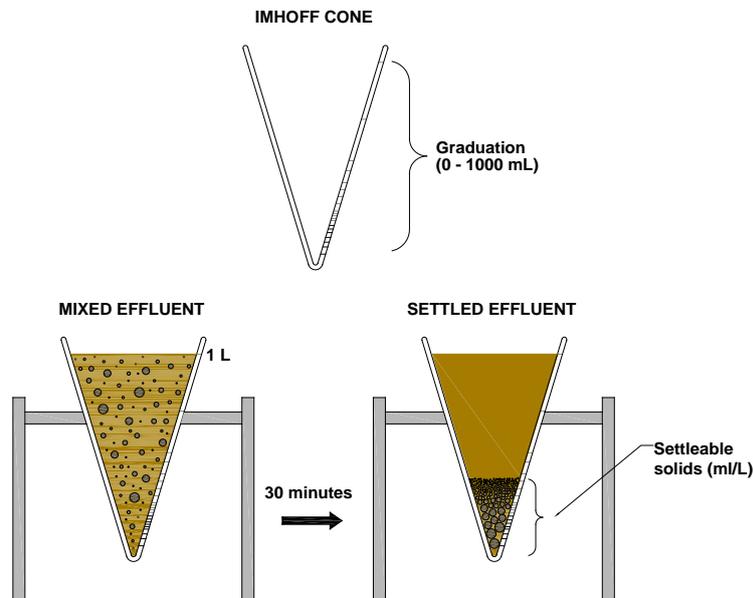
The main problem they cause is the large volume of sludge that forms as the solids settle. All this sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources.

If the waste water is to be discharged into surface water, the rate of flow will determine the distance the material is carried before settling on the stream or river bed. Even a thin layer of settled sludge can form a blanket that deprives sections of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition sets in.

In the course of effluent treatment, energetic mixing in the homogenization tank is essential in order to prevent suspended solids from settling at the bottom and possibly blinding air diffusers.

The analysis of the settleable solids content is very rapid and simple. One litre of the shaken raw effluent sample is left to settle for 30 minutes in a graduated Imhoff cone; the volume of thick, settled matter represents settleable solids in terms of ml/L. If effluent characteristics do not oscillate too much, the correlation between settleable and Total Suspended Solids, TSS can be established and the amount of TSS roughly estimated on the basis of this on-the-spot analysis.

SETTLEABLE SOLIDS



Semi-colloidal solids

Total Suspended Solids, TSS are made up of solids of two distinct characteristics:

- Solids with a rapid settling rate (settleable solids)
- Semi-colloidal solids

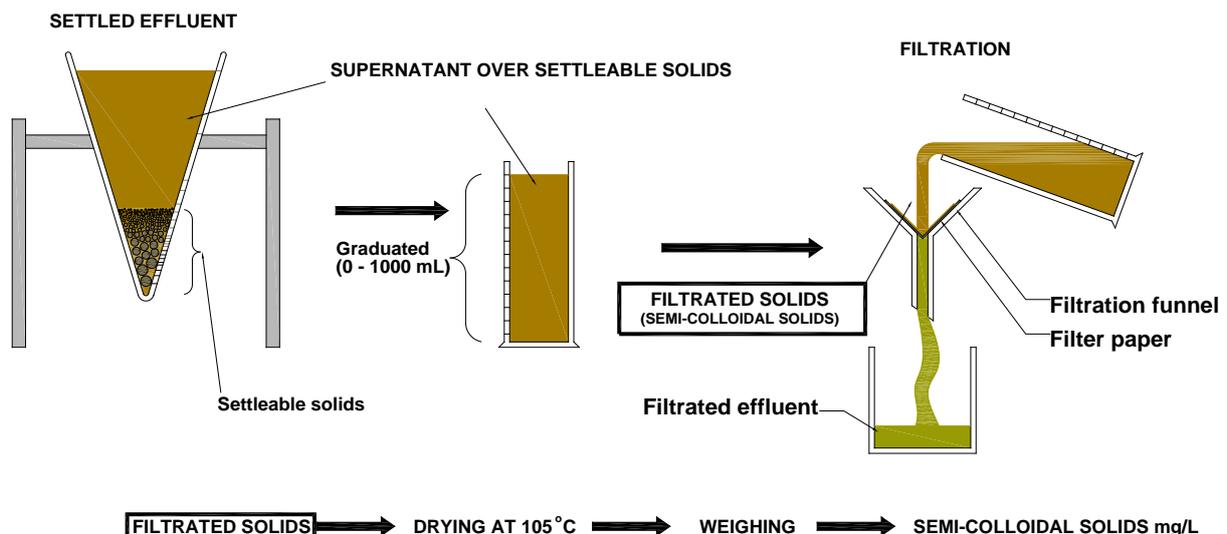
Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. They can, however, be filtered from solutions. Together with the more readily Settleable Solids, they thus comprise the Total Suspended Solids of an effluent that can be measured analytically.

Most of these solids are protein residues from the beamhouse operations - mainly liming processes; however, large quantities are also produced owing to poor uptake in vegetable tanning processes, another source being poor uptake during retanning.

Semi-colloidal solids normally do not cause pipeline or pump blockages and can be broken down over an extended period by bacterial digestion. Yet, it is important to have them removed by coagulation and flocculation in the course of primary treatment stage and thus reduce the load on and the cost of energy extensive biological treatment stage.

For day-to-day operations of an effluent treatment plant of primary interest is the amount of settleable solids. Sometimes, however, it is useful to determine the amount of semi-colloidal solids too: a known volume of effluent above the settled solids in the Imhoff cone is filtered through a filter paper which is then dried and re-weighed. The difference between this weight and that of the original paper gives the amount of semi-colloidal solids contained in the sample; subtracted from the Total Suspended Solids, TSS it gives the amount of settleable solids in terms of mg/L.

SEMI-COLLOIDAL SOLIDS



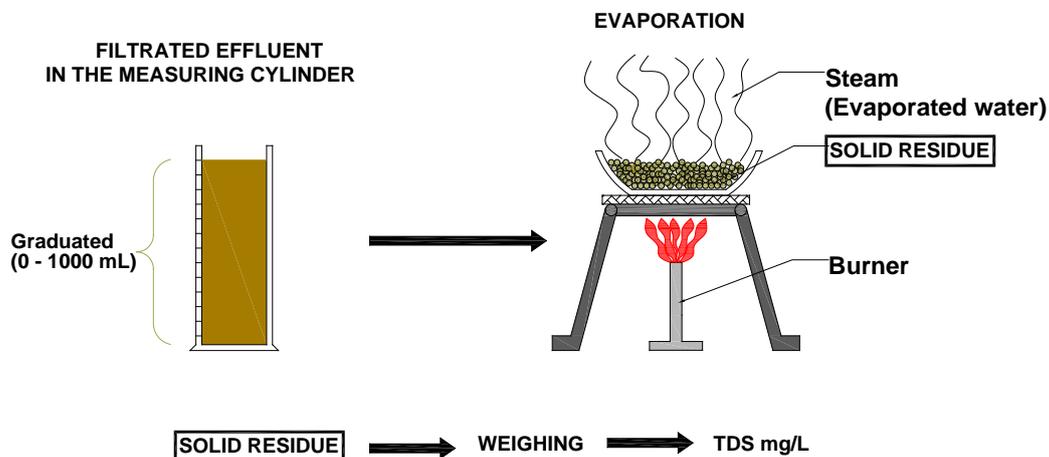
Total Dissolved Solids, TDS

Total solids, TS are made up of all measurable solids present in the effluent. Their quantity is determined by weighing the amount of solid residue left after evaporation of a known volume of mixed raw effluent and it is expressed in mg/L.

Total Solids, TS consist of two components i.e. insoluble, suspended (**Total Suspended Solids, TSS**) and dissolved (**Total Dissolved Solids, TDS**).

Total Dissolved Solids, TDS is a measure indicating the amount of all [inorganic](#) and [organic](#) substances dissolved in waste water; essentially, it is everything present in water other than pure H₂O and suspended solids. In the case of tannery effluents, the main relevant components are **sulphates** and **chlorides**. Very often TDS is colloquially referred to as salinity or salt.

TOTAL DISSOLVED SOLIDS



Sulphates (SO_4^{2-})

Sulphates in tannery effluent emanate from the use of sulphuric acid or auxiliary chemicals with high (sodium) sulphate content; chrome tanning powders and many synthetic retanning agents contain high levels of sodium sulphate.

Removal of sulphide in the effluent by aeration (beamhouse stream, homogenization tank) also generates (sodium) sulphates.

Sulphates cannot be removed completely from a solution by chemical means; normally, they either remain as sulphates in the effluent or are broken down by anaerobic bacteria to produce malodorous hydrogen sulphide. This process occurs very rapidly in effluent treatment plants, sewage systems and water courses, if effluents remain static.

This bacterial conversion to hydrogen sulphide in sewage systems results in the corrosion of metal parts, and unless sulphate-resistant concrete will gradually erode. If no breakdown occurs, the total concentration of salts in the surface water and groundwater is likely to increase.

Sulphate analysis is performed by adding barium chloride solution to a sample of filtered effluent. The sulphates are precipitated as barium sulphate and filtration; drying and calculation can determine the sulphate level.

Chlorides (Cl)

Chloride in effluent is chiefly sodium chloride originating from the large quantities of common salt used in hide and skin preservation and/or in the pickling process. Chlorides are 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.

High salt contents are only acceptable if the effluents are discharged into tidal/marine environments.

The level of salt as chloride under acid conditions can be determined by titrating a known volume of effluent with a silver nitrate solution, using potassium chromate as an indicator.

Under neutral or alkaline conditions, excess silver nitrate is added. This excess is then determined by retro-titration with potassium thiocyanate, using ferric alum as the indicator.

High TDS concentrations exert varying degrees of osmotic pressures and make otherwise fully treated waste water unfit for irrigation and livestock watering; also, high TDS often becomes lethal to the biological inhabitants of an aquatic environment.

The problem of salinity, together with utilisation and/or safe disposal of sludge is at the moment the biggest challenges of treatment of tannery effluents; the treatment does not affect (reduce) the TDS content, on the contrary, manganese sulphate (MnSO_4) added as a catalyst in the process of catalytic oxidation of sulphide and aluminium sulphate added as a coagulant slightly increase the TDS.

It should not be overlooked that some components of the TDS such as ammonium sulphate, lime, gypsum (calcium sulphate), magnesium, manganese as well as slow-release, high organic nitrogen products derived from hair can be beneficial since they are also components of fertilizers. Also, calcium and magnesium ions in tannery effluent ameliorate the adverse effect of sodium ions on soil structure. In any case, critical is the application rate.

For quick determination TDS meters are used, which in reality are conductivity meters that work by applying a voltage between two or more electrodes. Thus, TDS meters measure the conductivity of the solution containing dissolved [ionized](#) solids such as [salts](#) and based on that estimate the presence of TDS.

Dissolved organic solids such as sugar and microscopic solid particles such as colloids, do not significantly affect the conductivity of a solution and TDS meters do not include them in their reading.

Tannery effluent contains different inorganic (mostly good electrolytes) and organic substances (mostly bad electrolytes) in variable concentrations; however, under reasonably stable conditions in a particular tannery a satisfactory approximation of conductivity to TDS conversion ratio can be established.

Conductivity is typically expressed in [siemens](#) per meter (S/m), measured at 25° C; the old measure unit was S/cm or mS/cm (millisiemens per centimetre) sometimes μS , the relation being: $1 \mu\text{S/cm} = 100 \mu\text{S/m}$. TDS is normally given in mg/L

Conductivity meters can be portable, laboratory type or on-line i.e. integrated in the effluent treatment plant (ETP) for continuous measuring (mostly at the end of the process).

Discharge limits for Total Dissolved Solids, TDS (alternatively there are separate norms for chlorides and sulphates) vary greatly depending on specific local conditions (e.g. very stringent in arid countries) and the recipient (e.g. indirect discharge). In most cases tanneries are unable to meet them.

Here are some models of conductivity meters.



Portable conductivity meter



Laboratory conductivity meter



Process (on-line) conductivity meter

Sulphide (S²⁻)

The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide and from the breakdown of hair in the unhairing process. The sulphides pose many problems. Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterised by a smell of rotten eggs, a severe odour problem occurs.

Hydrogen sulphide is a flammable gas which burns with a blue flame, giving rise to sulphur dioxide, a highly irritating gas with a characteristic odour. Mixtures of hydrogen sulphide and air in the explosive range may explode violently; since the vapours are heavier than air, they may accumulate in depressions or spread over the ground.

Even a low level of exposure to the gas induces headaches and nausea, as well as possible damage to the eye. At higher levels, death can rapidly set in and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded. This is why strict segregation of beamhouse and tanyard streams is a must as well as early removal of sulphide in effluent, usually by catalytic oxidation.

Hydrogen sulphide gas is also fairly soluble. When absorbed, weak acids can form and cause corrosion. This weakens metal roofing, girders and building supports. In sewers, major problems can arise as metal fittings, structural reinforcements and, unless special cement is used, concrete pipework corrode.

If discharged to surface water, even low concentrations pose toxicological hazards. Sulphides can be oxidised into non-toxic compounds by certain bacteria in rivers; however, this creates oxygen demand which, if excessive, can harm aquatic life.

Sulphides in effluent can be determined in several ways. One of the most accurate methods relies on the acidification of suitable quantities of effluent to generate hydrogen sulphide. This is flushed through the apparatus using nitrogen gas, whereafter it is trapped and converted into zinc sulphide. The amount of sulphide is determined by titration and expressed in mgS²⁻/L.

Table 6 Poisoning effects of hydrogen sulphide gas (H₂S)

Exposure [ppm]	Time	Impact on unprotected person
0.03	No time limit	No effect
0.08 – 2.0	No time limit	(Mal)odour threshold
10	Up to 8 hours	No effect
15	Up to 15 minutes	Threshold limit value
15 - 200	Up to 15 minutes	Headache, nausea, general weakness, pain in legs
200 - 500	1 minute	Irritation of nose & throat, vertigo, blurring of vision, loss of consciousness lasting a few minutes
500 - 900	1 minute	Profound coma, convulsions, disorientation after recovery
> 900	1 minute	Instant coma and death

The globally prevailing discharge limit for surface waters for sulphide is 1 – 2 mg/L

Here are two models of portable hydrogen sulphide meters.



Chrome compounds; other metals

Despite extensive (re)search for alternatives, mineral tanning (chrome tanning) remains the prevailing method of leather tanning for quite obvious reasons: from technical, economic and environmental aspect it is simply the most superior method of leather making. Also, a very particular advantage of chrome tanned leather is its versatility.

Metal compounds are not biodegradable. They can thus be regarded as long term environmental features. Since they can also have accumulative properties, they are the subjects of close attention. Two forms of chrome are associated with the tanning industry, their properties being often confused. This, in turn often results in wrong perceptions, heated debates and undue pressures on the industry.

Chrome 3⁺ (trivalent chrome, chrome III)

Chromium is mainly found in waste from the chrome tanning process, sometimes it occurs as part of the retanning system but it can also be released from leathers during chrome-free retanning as well as from dyeing processes. Chrome released by “bleeding” in the course of sammying operation cannot be ignored either.

This chrome is discharged from processes in soluble form; however, when mixed with tannery waste waters from other processes (especially if proteins are present), the reaction is very rapid; precipitates are formed, mainly protein-chrome, which add to sludge generation.

Very fine, chrome stabilized colloids are also formed; in effect, the protein has been partially tanned. The components are thus highly resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

Once successfully broken down, chromium hydroxide precipitates and persists in the eco-systems.

Under certain conditions, mainly depending on pH, the chromium might remain in the solution; while chromium salts have no acute toxicity they are considered harmful to aquatic organisms and may have long-term adverse effect in aquatic environment. However, Cr III is less toxic than some other elements (Hg, Cd, Pb, Ni, Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form; Cr III compounds are almost insoluble so that they have a very low mobility in soils and are thus relatively unavailable to plants

Incineration of tannery sludge at elevated pH values (9-10), in the presence of excess of oxygen, can lead to conversion of Cr III to Cr VI. However newer methods allow to incinerate Cr(III) containing sludge without formation of Cr(VI).

It is disputed that Cr III is oxidised to Cr VI in the natural soil environment; organic material, Mn^{2+} , Fe^{2+} and Iron (Fe) reduce Cr VI to Cr III and some of these materials are being used to remediate Cr VI contaminated sites and groundwater.

The largest share of chromium used for tanning ends up in environment in leather products (footwear, apparel, leather goods) disposed of. However, somewhat paradoxically, in practice, it is chrome which in the course of effluent treatment is transferred to sludge that presently attracts considerable attention and causes most problems to tanners; its presence, under prevailing legislations, considerably limits the scope for utilisation and safe disposal of such sludges.

Chrome levels can be determined in a number of ways. The first stage, however, usually comprises boiling a known volume of sample with concentrated nitric acid to ensure complete solution of the chrome. After suitable dilution, the chromium level is determined by atomic absorption. Where high levels of chrome are expected, iodine/thiosulphate titrations are sometimes used. That technique, however, is inaccurate at low concentrations.

Chrome 6⁺ (hexavalent chrome, chrome VI)

Tannery effluents are unlikely to contain chromium in this form. Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative.

In recent years it has been noticed that under certain conditions (oxidative environment – presence of unsaturated fats and fatliquors, aging) chrome VI can be formed in finished leather and leather articles whereas the presence of vegetable (re)tanning agents might help preventing it.

Cr VI can be toxic and carcinogenic although low levels can be tolerated; its carcinogenicity is respiratory and is work related and due to welding and inhalation of some Cr VI powders.

Practically, the only real health risk associated with presence of chrome VI in leather and articles made of leather is the allergy due to extended contact with skin (e.g. gloves, footwear); again it is estimated the number of people affected is considerably below 1 % of population, the threshold considered to raise concerns.

Yet, some brands and eco-labels insist on Chrome VI presence not exceeding the analytical detection level of 3 ppm (see below).

Analysis is highly specialised. According to EN ISO Method 17075 (photometric analysis) , the first step is leaching of soluble chromium VI from the ground sample (2 g) at pH 7,5-8,0 (phosphate buffer) under inert gas (argon or nitrogen) by shaking for 3 h, followed by filtration through a membrane filter and reaction with 1,5-diphenyl-carbazide to give a red/violet complex. The photometrical measurement is at 540 nm, the chromium content given in mg·kg⁻¹ (on dry matter). Determination limit: 3 mg·kg⁻¹ (i.e. 3 ppm)

The amount of chrome and the relevant norm is given in mg/L, usually separately for chrome III and chrome VI and/or as the Total chrome, mg/L. A typical, globally prevailing discharge limit for surface waters for chromium is 1.5 – 2.0 mg/L

Other metals

Other metals which might be discharged from tanneries and whose discharge may be subject to statutory limits include **aluminium** and **zirconium**.

Depending on the chemical species, these metals have differing toxicities that are also affected by the presence of other organic matter, complexing agents and the pH of the water. Aluminium, in particular, appears to inhibit the growth of green algae and crustaceans are sensitive to low concentrations. **Cadmium**, sometimes used in yellow pigments, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If present in drinking water, it can induce brittleness in bones.

Oxygen demand

Biochemical Oxygen Demand (BOD₅) and Chemical Oxygen Demand (COD)

Most chemical compounds in effluents are broken down by bacterial action into more simple components. Oxygen is required for both the survival of these bacteria (aerobic bacteria) and the breakdown of the compounds. Depending on their composition, this breakdown can be quite rapid or may take a very long time.

If effluent containing chemical compounds with a high oxygen demand is discharged directly into surface water, the sensitive balance maintained in the water is upset; aerobic micro-organisms consume the oxygen present in the water causing oxygen dependent plants, bacteria, fish as well as the river or stream itself to die. The ultimate outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions and unpleasant smell.

While a healthy river can tolerate substances with low levels of oxygen demand, the pollution load created by tanneries is excessive and the effluent requires treatment prior to discharge. In addition to physical-chemical treatment this is usually achieved by using microorganisms normally present in the environment, under controlled conditions in a biological process demanding high levels of oxygen. Oxygen induction is achieved by blowing large volumes of air into the effluent. Energy consumption and, as a corollary, capital and operational costs are very high.

As the result of degradation of chemical compounds water and carbon dioxide are produced in large volumes; the process, however, depends upon bacterial growth. As the bacteria die, they form sludge that has to be treated and ultimately disposed of. This sludge has high water content and is often quite difficult to dewater, thus adding considerably to the treatment costs.

To assess an effluent's negative impact on water recipient as well as to estimate the costs of treatment, the oxygen demand of raw effluent needs is determined by using two parameters: Biochemical oxygen demand (BOD₅) and Chemical oxygen demand (COD).

Biochemical Oxygen Demand (BOD₅)

BOD is the quantity of oxygen required during the stabilisation of decomposable organic and oxidizable inorganic matter by aerobic biological action at standard conditions; instead of 20 usually over only five days.

It means the more organic matter in effluent, the greater the BOD, the lower the amount of dissolved oxygen available for fishes and thus more extensive effluent treatment needed before discharge.

BOD analysis is extremely complex, sensitive and has serious limitations. Two methods are widely accepted. The dilution method mimics biodegradation in nature: after removal of settleable solids the sample is diluted in water, pH adjusted, seeded with bacteria (often settled sewage effluent) and incubated in tightly closed bottles in the dark for five days at 20°C. During this time the microorganisms break down the organic matter and consume the oxygen. The amount of remaining oxygen is determined either by means of an oxygen meter or by analysis and the BOD₅ calculated by comparison to the blank effluent-free samples.

This method of detection has various weaknesses and the results can be misleading. The bacterial cultures can vary, some compounds will only be partially broken down and some not significantly

affected: certain retanning agents, synthetic fatliquors, dyes and residual proteins from hair solubilisation. Also, the breakdown period for vegetable tanning wastes can be up to 20 days.

The manometric – respirometric method is faster and simpler as there is no dilution, seeding and no parallel, blank sample but it is even less accurate and reliable. Again, in the course of degradation in the dark, the carbonaceous matter consumes the oxygen present in the effluent. However, here an alkali absorbs the carbon dioxide developed in the process; the drop in pressure in the sealed container equipped with a sensor can be continuously read.

Chemical Oxygen Demand (COD)

COD is the quantity of oxygen consumed for the total oxidation of the oxidizable matter (organic and inorganic) with dichromate as the oxidising agent. The COD is always greater than its BOD.

This method measures the oxygen required to oxidise the effluent sample wholly. It sets a value for the materials that would normally be digested in the BOD₅ analysis, the longer term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity.

Effluent sample is boiled with a powerful oxidising agent (potassium dichromate) and sulphuric acid. As the effluent components oxidise, they use oxygen from the potassium dichromate, the amount used being determined by titration.

This method is often favoured over BOD as it provides rapid results within a few hours instead of days and it is more reliable and cost effective. If the effluent characteristics remain relatively uniform over a long period, a ratio between BOD and COD may be determined and the COD test can be used instead of the BOD test.

As a rule of thumb, the ratio between COD: BOD is 2.5:1, although in untreated effluent samples variations can be found as great as 2:1 and 3:1. This depends on the chemicals used in the different leather making processes and their rate of biodegradability.

Both, BOD and COD analyses are based on settled effluent, not filtered. This means that the semi-colloidal material that forms part of the suspended solids is also included in the BOD and COD determinations. Normally 1 mg/l suspended solids will generate a COD increase of approximately 1.5 mg/l.

In contrast to BOD and COD as indicators of pollution, high **Dissolved Oxygen, DO** can be taken as a sign of good health of a natural water system in which oxygen supply (by absorption from the atmosphere and from plants as a result of photosynthesis) is not outstripped by oxygen consumption (respiration by aquatic animals, decomposition and chemical reactions). In effluent treatment plants DO is the key indicator of the quality of aeration during the biological stage of the process.

The commonly used test method is according to Winkler principle and DO is expressed either in milligrams per litre (mg/L) or "percent saturation" (the amount of oxygen relative to the total amount of oxygen that the water can hold at that temperature).

The globally prevailing discharge norms for surface waters for COD and BOD₅ are within the range of 125 – 250 mg/L and 30 – 40 mg/L respectively.



BOD dispensable bottles



Incubator for BOD analysis by dilution method



BOD manometric respirometer



Instrument for BOD analysis by respirometric method



A COD measuring set



COD digestion apparatus

Nitrogen

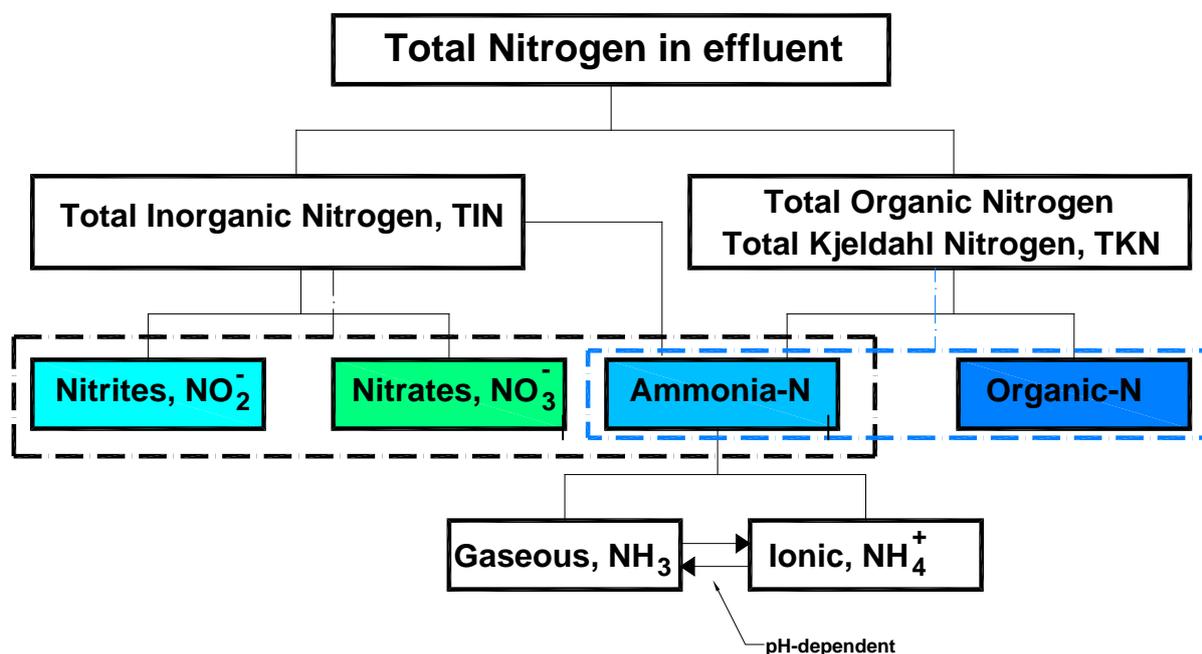
Nitrogen is essential constituent of all amino acids which in turn build proteins; it is also present in the nucleic acids (DNA and RNA) and thus essential for all life on earth.

More specifically, (water) plants require nitrogen in order to grow. Yet, excessive amounts of nitrogen in waste waters pose very serious problems.

High levels of nitrogen over-stimulate growth: water-based plants and algae grow too rapidly so that waterways become clogged and flows are impaired. Also, as the plants die, decomposition of large amounts of organic matter leads to depletion of oxygen available in the water body. Plants, fish and aerobic bacteria die and ultimately anaerobic conditions and bad smell develop.

Secondly, in the process of effluent treatment, excess of nitrogen is removed by combining intensive aerobic (nitrification) and anoxic (denitrification) biological treatment. The oxygen demand is very high, thus leading to correspondingly high operational and energy costs. Typically, some 40% of the oxygen requirements are spent on removing the nitrogen component.

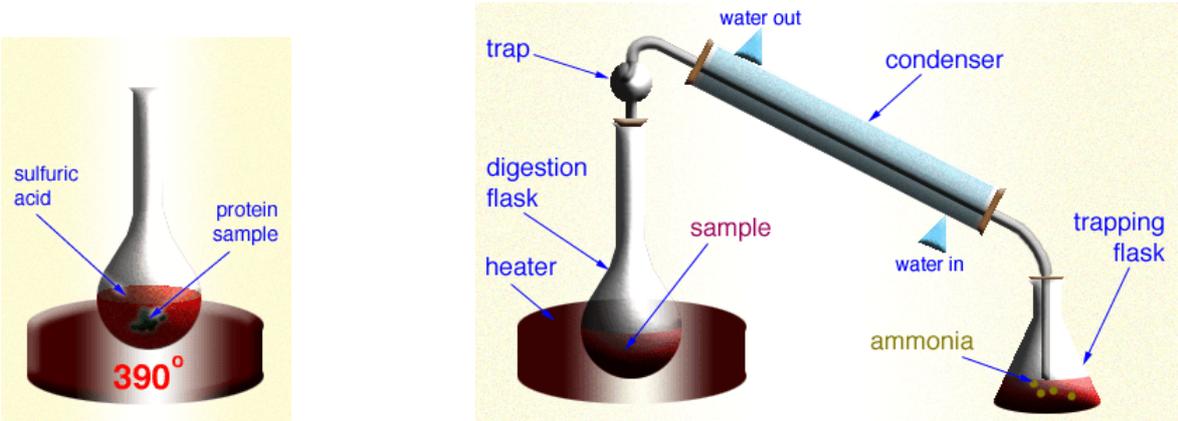
Two main sources of nitrogen in effluent are i) proteinaceous materials emanating from hide structure and released during liming/unhairing operations and ii) ammonia salts used for deliming (Pollution prevention technologies such as carbon dioxide deliming are focused on the latter). Both components are contained in several waste streams and very often they have to be differentiated.



Total Kjeldahl Nitrogen (TKN, mg/L) is the 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 ammonia/ammonium salts. Total Inorganic Nitrogen, TIN, i.e. Total Nitrogen – Total Organic Nitrogen (TKN) is seldom asked for. The pH directly defines whether it is ammonia (NH₃) or ammonium (NH₄⁺) form.

During the first stage in the analysis by the Kjeldahl method the nitrogenous matter is boiled with sulphuric acid to form ammonium compounds. In a second stage, the ammonia is released on being

boiled with sodium hydroxide, and subsequently trapped in a boric acid solution. The level of ammonia released is determined by titration, and its value calculated as nitrogen.

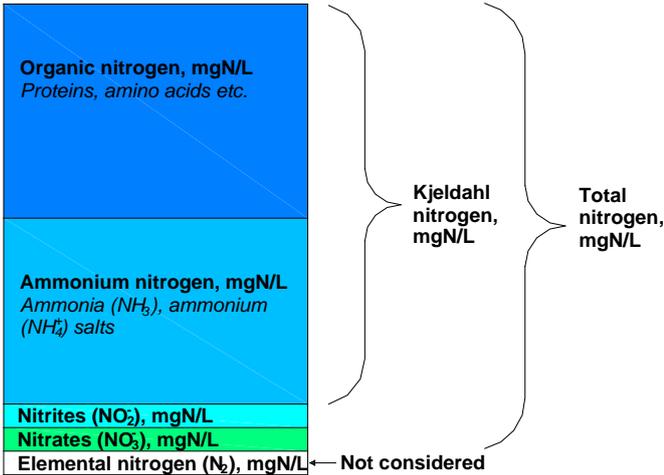


Ammonium content as nitrogen (N)

This value is also sometimes specified in discharge limits. Ammonium compounds are part of TKN and the problems associated with rapid plant growth and oxygen demand are also very similar. These compounds are mostly the outcome of the deliming process, some emanate from break up of proteins/aminoacids. The analysis is similar to that of TKN, but omits the initial digestion stage thus excluding the nitrogen component resulting from protein wastes.

As a rule, **nitrites (NO₂⁻)** and **nitrates (NO₃⁻)** appears only as stages in converting all excess nitrogen to inert N₂ gas released into atmosphere.

NITROGEN BALANCE IN THE TANNERY WASTEWATER
Approximate scale



The norm for discharge into surface waters for Total Kjeldahl Nitrogen, TKN is locally specific: from less than 50 mg/L in industrialized to 100 mg/L in some developing countries.

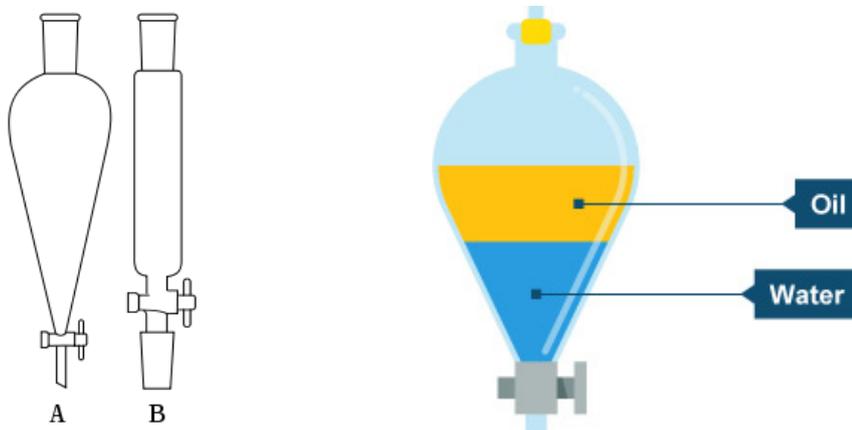
Oils and grease

During leather manufacture, natural oils and grease are released from within the skin structure whereas carefully chosen fatliquors are added as lubricants and/or to lend finished leather a desired feel as well as some water repellence. If fatliquor exhaustion is poor, some fatty substances may be produced through inter-reaction when waste waters mingle.

Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems.

If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is significantly reduced. If such fatty substances emulgate, they create a very high oxygen demand on account of their bio-degradability.

The presence of oils and grease is determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the water phase. This solvent dissolves fatty matter, and a quantity can be drawn off and evaporated until dry. The residual grease can be weighed and calculated; the content is expressed in mg/L.



Separation funnels



Oil and water separation in a funnel

Organic solvents in waste water

Traditionally, organic solvents have been mostly applied in degreasing and finishing operations; due to occupational and health hazard most of them pose, their use in recent years has been significantly reduced, primarily by wider acceptance of predominantly water based finishing.

Solvents in effluents discharged to surface waters can form a microfilm on the water surface, thus inhibiting the uptake of oxygen. Solvents break down in a variety of ways; some inhibit bacterial activity and remain in the eco-system for extended periods of time. Analysis is highly specialised.

As a rule, environmental authorities more strictly limit and monitor presence of organic solvents in air emissions, especially in tanneries located close to residential areas (see Air emissions).

pH value

The pH of the effluent is also very important for its possible negative impact on the environment. If the surface water pH shifts too far either way from the pH range of 6.5 - 7.5, sensitive fish and plant life are susceptible to loss; here it should be remembered that the pH scale is not linear but logarithmic in which two adjacent values increase or decrease by a factor of 10. Thus, for example, a pH of 8 is ten times more alkaline than a pH of 7 whereas a pH of 3 is ten times more acidic than a pH of 4.

Mixing of alkaline (beamhouse) and acidic (tanyard) streams results in composite effluent of pH 6-9 which does not change much in the course of treatment despite acidity of most coagulants (e.g. alum) and carbon dioxide and nitrates developed during the biological treatment stage. Lime dosing arrangements are a standard for possible pH adjustments both in the equalisation and biological tank.

Acceptable limits for discharge of waste waters to both surface waters and sewers vary, ranging between from pH 5.5 to 10.0. Although stricter limits are often set, greater tolerance is shown towards higher pH (alkalinity) since carbon dioxide from the atmosphere or from biological processes in healthy surface water systems tends to lower pH levels very effectively to neutral conditions

Municipal and common treatment plants prefer discharges to be more alkaline as it reduces the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulphide evolution is minimised. When biological processes are included as part of the treatment, the pH is lowered to more neutral conditions by carbon dioxide so evolved.

There is a wide range of benchtop, on-line and portable pH meters with detailed instructions on use (calibration, temperature compensation etc.).



Benchtop and portable pH meters

Substances of Very High Concern (SVHC)

There are substances which are considered extremely harmful for being **carcinogenic, mutagenic, toxic for reproduction, persistent, bioaccumulative and toxic, very persistent and very bioaccumulative**, as having **endocrine glands disrupting properties** or having a **combination of the mentioned properties**. Some of such substances might be used in leather processing too.

In the EU Registration, Evaluation and Assessment of Chemicals, REACH system, such substances are classified as Substances of Very High Concern (SVHC); they are included in the European Chemical Agency (ECHA) Candidate List. The list is continuously expanded with substances for which there is sufficient scientific evidence for falling into some of the listed categories. Some believe that ultimately the list might include more than a thousand substances.

In that context it is useful to know that there is also the SIN (Substitute It Now) List promoted by an NGO Advisory Committee which includes (amongst others) WWF, Friends of the Earth and Greenpeace. This is a list of substances that in the view of the Advisory Committee fulfil the criteria for Substance of Very High Concern as defined by REACH. Although it certainly not official, the list is used by NGOs to lobby Member States for proposing substances for inclusion into the 'Candidate List'.

The Stockholm Convention is a global treaty that specifically deals with persistent organic pollutants (POPs) - chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife.

At the moment concerns about the Substances of Very High Concern (SVHC) are primarily focussed on their possible presence in leather and leather products. In many countries there are no specific norms for SVHC in tannery effluents; also, according to recent research in France only one SVHC was found in treated effluent. Nevertheless, it is an issue likely to be given more importance in the future; the same applies to POPs.

Air pollutants, VOCs

Air pollutants are increasingly coming under the scrutiny of legislators. As in the case of waste water, environmental protection agencies often establish discharge limits taking into account the absorption capacity of the receiving environment. Also, monitoring and enforcement are normally stricter for tanneries located close to residential areas which is not surprising: the (mal)odour intensity rises with concentration according to the logarithmic scale.

The main air pollutants are **hydrogen sulphide (H₂S)**, **sulphur dioxide (SO₂)**, **ammonia (NH₃)** and **malodours**, but there are also acid **fumes**, **phenols**, **formaldehyde** and **fine dust**.

A special category are **volatile organic carbons, VOC** that in leather processing normally emanate from various organic solvents used in finishing.

VOCs are the carbon-based chemicals that vaporize at room temperature and, when in air, predominantly exist in the vapour phase. The direct negative impact of VOCs is for example the carcinogenic effect of benzene. The indirect negative impact is due to their photochemical ozone creation potential (POCP), i.e. their reaction with nitrogen oxides in the presence of sunlight to form photochemical oxidants.

The discharge norms in terms of mg/m³ are usually linked to emission rate expressed in g/h (see the table below).

Table 7 **EU air emission limits**

Pollutant	Emission mg/m ³
Hydrogen sulphide, H ₂ S	2-5 at 50 g/h mass flow rate
Sulphur dioxide, SO ₂	500 at 5,000 g/h mass flow rate
Ammonia	10-30 at 300 g/h mass flow rate
Volatile organic carbons, VOC Category I	20 at 100 g/h mass flow rate
Volatile organic carbons, VOC Category II	150 at 2,000-3,000 g/h mass flow rate
Volatile organic carbons, VOC Category III	300 at 3,000-6,000 g/h mass flow rate

The use of volatile chlorofluorocarbons (CFCs) and other halogenated hydrocarbons is banned in most countries, but halogenated biocides are still used.

In European Union, EU, the following are the current VOC emission limits related to organic solvent consumption in finishing:

10-25 t/year: 85 g/m² of finished leather produced
 More than 25 t/year: 75 g/m² of finished leather produced.

Even more complex and strict are regulations for emissions in the workplace. The presence and the concentration of the hazardous air pollutants is here regulated in terms of Threshold Limit Values (TLV), defined as Time Weighted Average (TWA, i.e. eight hours of continuous exposure), as well as Short Term Exposure Limit (STEL).

In the market there are many models of fixed and portable gas meters; VOC analysis are rather sophisticated, the reliability and selectivity of VOC sensors still an issue. Monitoring is on continuous, in regular intervals and/or at random basis.

For illustration, here are two models of H₂S meters and two models of VOC meters.



Toxicity of effluent components

The toxicity of effluent components following dilution in surface waters is a complex subject. The lack of specific data is due to the wide variety of aquatic life, the nature of individual components and their degradation rate, either in suspension or as part of sediment. It is not possible to attain a high degree of specificity for complex and multiple effluent components, whose effects on fish, invertebrates, algae and daphnia (a tiny crustacean often used toxicity tests) can be quite different.

A measure of toxicity can be expressed as LD50, representing the dose which will kill 50 per cent of a sample species. Not every species reacts to the same degree to a given exposure, and the type of response to an equal dose of a chemical may differ widely. When values are given, the species under test should be stated and the time period taken for evaluation should normally be 24 or 96 hours or 14 days.

Environmental quality standards are also used to monitor the protection of aquatic life, based on fate, behaviour and aquatic toxicity; they may be defined as the concentration of a substance which must not be exceeded if a specific use of the aquatic environment is to be maintained.

The metals that might be present in tannery effluents (viz. chromium, aluminium and perhaps zirconium) are all classified as having a 'high'/'moderately acute' or 'chronic' toxic effect upon organic life and being 'accumulative'. An 'acute' effect may be defined as one that has a specific effect on fish within 96 hours, whereas a 'chronic' effect may need a 21 day test period or even involve complete life cycles, the determination of egg-counts and fertility factors.

The toxicity of many metals also varies according to the pH level, temperature and water hardness. Where Cr^{3+} is concerned, investigations have been performed on fish (unspecified) under conditions of exposure insufficient to cause severe toxicity, yet sufficient to cause visible changes in behaviour. These dosages were 0.2 mg/l. It is understood however, that daphnia are even more susceptible, thus posing a potential hazard to the food chain for fish.

Although not used in leather processing, zinc and copper are described as having a 'high/acute' and 'chronic' toxic effect on aquatic life. The maximum levels are 0.3 mg/l total and 0.04 mg/l (dissolved) respectively as given in the standards set by the EU in its Fish Directives for salmon. Similar toxicity definitions apply to Cr^{3+} , and it is stated that dosages of 0.2 mg/l induce behavioural change in fish (unspecified). In the absence of more specific data, loadings of this order might be considered maximum permissible values for surface waters.

No limits are set for COD, as substances (and toxicity) cannot be specified. Other limits found in the standards set by the EU in its Fish Directives are presented below:

Suspended solids	< 25 mg/l
BOD ₅	< 5 mg/l
Ammonia (as NH ₃)	< 0.025 mg/l
Kjeldahl nitrogen	< 0.78 mg/l

There are no values for sulphides, but their presence is reflected in the BOD analysis.

Direct toxicity assessment

Chemical/biological analyses of the toxicity limits for specific effluent components have served as a basis for determining discharge limits into recipient waters. These techniques, however, cannot always account for:

- Unexpected toxic effects from the reaction of seemingly innocuous substances upon admixture; and
- Some substances being toxic to aquatic life at levels too low to be detected by normal methods.

A new technique that departs from the traditional approach is under investigation in the United States and Europe. It involves taking samples of the effluent and testing the effect at various dilutions on organisms of increasing complexity, such as algae, daphnia, water fleas and fish that might be found in surface waters. Known as direct toxicity assessment, this technique should provide a means of testing the effects of complex discharges under conditions near to real life.

Where tannery effluents are discharged directly into sewers, the responsibility for final discharge will be borne by the municipality. Where industrial wastes are directly received into surface waters, however, the industry might be directly affected and investigations might lead to a redefinition of limits at both the local and national levels.