OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

23440

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION (UNIDO)

Technical Information on Industrial Processes

POLLUTANTS IN TANNERY EFFLUENT

International Scenario on Environmental Regulations and Compliance

by

M. Bosnic, J. Buljan, R. P. Daniels, S. Rajamani

Leather Industry Pollution Control Experts

under the UNIDO technical assistance project SF/EGY/97/167
managed by
Ferenc Schmél
Industrial Development Officer

Vienna, 2003

The original document was prepared in 1999.

Abbreviations

approx. : approximately
avg. : average
BOD_5 : Biochemical Oxygen Demand, 5 days
Cl : Chloride
COD : Chemical Oxygen Demand
Cr III : trivalent chromium
diam. : diameter
DS : dry solids
DW : dry weight
CETP : Common Effluent Treatment Plant
h : hour(s)
H : height
ha : hectare (=10,000 m^2)
m^2 : square meter
m^3 : cubic meter (=1000 litres)
mg/l : milligrams per litre
max. : maximum
meq/l : milliequivalents per litre
min. : minute(s)
ml/l : millilitres per litre
MWh : Megawatt per hour
O & G : oil and grease
pc (pcs) : piece (pieces)
pH : logarithm of the reciprocal of the hydrogen ion concentration
PW : pelt weight
RMW : raw material weight (green-wet salted weight)
S^{2-} : Sulfide (as S)
sec. : seconds
SO_4 : Sulphate
Sq.ft square foot (=0.0929 m^2)
SS : suspended solids
t : metric ton (=1000 kg)
TDS : total dissolved solids
CRP : Chrome recovery plant
W (kW) : watt (kilowatt)

TABLE OF CONTENTS

EXECUTIVE SUMMARY 6

1. INTRODUCTION 8

2. TANNING PROCESS AND WASTE WATER DISCHARGE 9
    2.1 The Tanning Processes 9
    2.2 Waste water discharge 9

3. SOURCES OF POLLUTION 11

4. ESTIMATION OF POLLUTION DISCHARGE 16

5. INTERNATIONAL SCENARIO ON ENVIRONMENTAL REGULATIONS 18
    5.1 General 18
    5.2 Environmental Standards 18

6. POLLUTION CONTROL REQUIREMENTS AND EFFLUENT MANAGEMENT 20
    6.1. Segregation of streams and pre-treatment in tanneries 21
    6.2. Primary (physical-chemical) treatment units 22
    6.3. Secondary biological treatment units 22

7. EXPERIENCES IN COMPLIANCE OF REGULATIONS AND IN SETTING UP OF TREATMENT PLANTS 23
    7.1 Treatment Plant Capacities 23
    7.2 Design of Treatment Plants 23
    7.3 Sectional of Site and Appropriate Treatment Technology 23
    7.4 Cost Estimate and Financing 23
    7.5 Equipment & Materials of Construction 24
    7.6 Operation and Maintenance of Effluent treatment system 24

8. VIEWS AND SUGGESTIONS 26

Annexure 1
Pollution parameters of tannery effluent and their estimation

Annexure 2
Pollution Limits For Discharge of Effluents into Water Bodies and Sewers
Argentina, Australia, Austria, Brazil, China, Colombia, Costa Rica, Croatia, Czech Republic, Denmark, Egypt, Finland, France, Germany, Greece, Hungary, India, Indonesia, Iran, Ireland, Italy, Japan, Kenya, Mexico, Netherlands, New Zealand, Nicaragua, Pakistan, Philippines, Poland, South Africa, Spain, Sri Lanka, Switzerland, Tanzania, Thailand, Tunisia, Turkey, Uganda, UK, Uruguay, USA, Venezuela, Vietnam, Zambia and Zimbabwe

Annexure 3
Fig. 3.1. Process flow diagram of tanning operation
Fig. 3.2. Pollution Discharge per ton of hides/skins processed from raw to finish
Fig. 3.3. Tannery Effluent Treatment System

EXECUTIVE SUMMARY

Leather processing has emerged as an important economic activity in several developed countries. It has been estimated that currently about 1.8 billion m^2 of leather is made annually in the world. Bulk of leather production is carried out in developing countries: particularly in Asia and Africa partially because of the high labour intensity of the processes involved in the conversion of hides and skins into leather.

The total processing capacity of the world tanning industry is more than 10 million t of hides and skins per year. The processes employed in the manufacture of leather in several developing countries remain traditional, often not optimized for chemical and water usage. The estimated total wastewater discharge from tanneries is about 400 million m^3/year. The environment is under increasing pressures from solid and liquid wastes as by-products from leather manufacture and tannery effluent create significant pollution unless there has been a form of treatment before discharge. The industry has gained a negative image in the society with respect to its pollution potential and therefore the leather processing activity is facing a serious challenge.

Tannery waste management has become a matter of increasing concern. Environmental regulations and laws in many developing countries have been passed mostly during the last decade. But the compliance has not always been practical, either because the laws either too ambitious or unrealistic in certain parameters, or because they have lacked effective instrumentation and institutional support. Some environmental laws have not succeeded as they do not match the technical requirements and economic reality of the country or region, or because they do not take the institutional capabilities of the society that has to implement them into consideration.

The inability to comply with environmental regulations has posed a serious threat to the existence of the leather sector in recent times. There is now an urgent need to assess the extent of pollution, identify the sources, quantify the levels, carry out process audit and evolve adequate mitigation strategies in leather processing industry. These are essential steps if the leather processing is to be rendered environmentally sustainable.

It is important to first carefully analyze the effluent generated in different stages of leather processing. This will help estimation of various pollutants discharged in wastewater streams that would, in turn, help in evolving effective strategies for mitigating the pollution related problems faced by the leather industry. The focal theme of this paper is to present major tanning processes adopted by the tanneries in developing countries, volume of wastewater discharged, analytical data of the essential parameters, their definition and estimation of pollution load discharged at various stages of process and their environmental impact, compilation and updating of the Environmental regulations and pollution limits for discharge of effluents into water bodies and sewers from 46 countries covering Argentina, Australia, Austria, Brazil, China, Colombia, Costa Rica, Croatia, Czech Republic, Denmark, Egypt, Finland, France, Germany, Greece, Hungary, India, Indonesia, Iran, Ireland, Italy, Japan, Kenya, Mexico, Netherlands, New Zealand, Nicaragua, Pakistan, Philippines, Poland, South Africa, Spain, Sri Lanka, Switzerland, Tanzania, Thailand, Tunisia, Turkey, Uganda, UK, Uruguay, USA, Venezuela, Vietnam, Zambia and Zimbabwe. Technologies broadly adopted in treatment of tannery effluent for compliance of the regulations and their techno-economic viability in achieving the prescribed pollution limits are also included in the report.

1. INTRODUCTION

Leather processing has emerged as an important economic activity in several developed countries. The total processing capacity of the world tanning industry is more than 10 million t of hides and skins per year. It has been estimated that currently about 1.8 billion m^2 of leather is made annually in the world. Bulk of leather production is carried out in developing countries: particularly in Asia and Africa partially because of the high labour intensity of the processes involved in the conversion of hides and skins into leather.

The processes employed in the manufacture of leather in several developing countries remain traditional, often not optimized for chemical and water usage. The estimated total wastewater discharge from tanneries is about 400 million m^3/year. The environment is under increasing pressures from solid and liquid wastes as by-products from leather manufacture and tannery effluent create significant pollution unless there has been a form of treatment before discharge. The industry has gained a negative image in the society with respect to its pollution potential and therefore the leather processing activity is facing a serious challenge.

Environmental regulations and laws in many developing countries have been passed rapidly during the last decade. But the compliance has not always been practical, either because the laws either too ambitious or unrealistic, or because they have lacked effective instrumentation and institutional support. Some environmental laws have not succeeded as they do not match the technical requirements and economic reality of the country or region, or because they do not take the institutional capabilities of the society that has to implement them into consideration.

The inability to comply with environmental regulations has posed a serious threat to the existence of the leather sector in recent times. There is now an urgent need to assess the extent of pollution, identify the sources, quantify the levels, carry out process audit and evolve adequate mitigation strategies in leather processing industry. These are essential steps if the leather processing is to be rendered environmentally sustainable.

It is important to first carefully analyze the effluent generated in different stages of leather processing. This will help estimation of various pollutants discharged in wastewater streams that would, in turn, help in evolving effective strategies for mitigating the pollution related problems faced by the leather industry. The focal theme of this paper is to present major tanning processes adopted by the tanneries in developing countries, volume of wastewater discharge, analytical data of the essential parameters, their definition and estimation of pollution load generated at various stages of process and of composite streams, compilation and updating of the environmental regulations and pollution limits for discharge of effluents into water bodies and sewers from 46 countries, compliance of the regulations including technologies broadly adopted in treatment of tannery effluent and their techno-economical viability in achieving the prescribed pollution limits.

2. TANNING PROCESS AND WASTE WATER DISCHARGE

The tanneries predominantly process sheep and goat skins, cow and buffalo hides in most Asian and African countries and skins of other animals like pig, camel, horse etc in limited tanneries depending upon the availability of raw material, local regulations and market. They practice both vegetable tanning using barks, nuts and vegetable tan extract and mostly chrome tanning using Basic Chromium Sulphate (BCS) and other chemicals. In order to easily draw large quantity of water required for the tanning processes, most of the tanneries are located near water resources like riverbanks.

In leather processing, the basic strategy is to clean skin of the unwanted inter-fibrillary material through a set of pre-tanning operations generally called beamhouse operations, preserve permanently by means of tanning and add aesthetic properties during post tanning stages.

2.1 The Tanning Processes

Processing of wet or salted hides/skins is carried out at different stages depending on the availability of machinery, hides/skins, labour and water. Only in few tanneries generally located near cities with organized slaughter house process fresh hides and skins. The processing of wet salted hides/skins may be grouped into four major categories namely,

(i) Processing of wet or dry salted hides/skins into vegetable tanned semi-finished leather (raw to East India (EI) Leather).

(ii) Processing of wet or dry salted hides and skins into chrome tanned semi finished leather (Raw to wet-blue).

(iii) Processing of wet or dry salted hides and skins into finished leather (raw to finish).

(iv) Processing of vegetables tanned semi-finished leather and/or chrome tanned semi finished leather to finished leather.

The beam house operations in the process of hides and skins like soaking, liming, fleshing, de-liming, etc. are common irrespective of the type of tanning process carried out subsequently. The overall tanning operations are shown in a process flow diagram and attached as *Annexure 3*.

Tanneries are generally located close to a watercourse; it may be river, tank, ground water sources (wells and galleries). The sumps built inside the units serve as storage tanks. Overhead tanks with planned network of water mains with flow meter are seldom seen. As a result, the budgeting of water for various uses in the processes and washings is not managed scientifically.

2.2 Waste water discharge

Though the quantity of water use and wastewater discharge fluctuate in a wider range, the following most probable range was estimated for conventional tanning process including washings and wastage.

Table 1. **Wastewater discharged from different tanning process**

No.	*Process*	*Volume of waste water discharged in m^3/t of wet salted raw material processed*	
		Hides	Skins
1.	Raw to E.I	15-22	18-25
2.	Raw to wet-blue	18-25	20-30
3.	Raw to finishing	30-40	35-45
4.	E.I. to finishing	12-18 (40-60 in terms of EI wt)	12-18 (40-60 in terms of EI wt)
5.	Wetblue to finishing	10-15 (20-30 in terms of wet blue wt)	10-15 (20-30 in terms of wet blue wt)

It can be observed that while processing wet salted cow or buffalo hides up to E.I or wet-blue stage about 20% less water is used on raw weight basis when compared with the processing of goat or sheep skins.

3. SOURCES OF POLLUTION

The volume of wastewater discharge and typical characteristics of main sectional streams: soaking, liming, reliming, deliming, pickling, chrome tanning, neutralization, re-tanning, dyeing and composited streams are given in *Table 2*. The pollution load in terms of kg/t of raw material processed from raw to finishing is given in *Table 3* and shown as graph in *Annexure 3*.

Table 2. **Characteristics of tannery wastewater from raw to finishing process**

Parameter	*Soaking*	*Liming/re-liming*	*Deliming*	*Pickling*	*Chrome tanning*	*Neutralization*	*Rechroming dyeing fat liquor & wet finish*	*Composite (including washings)*
Volume of effluent/t of hides/skins	5-9 m^3	3-5 m^3	1.5 - 2 m^3	0.5-1 m^3	1-2 m^3	2-3 m^3	3-6 m^3	30-40 m^3
PH	7.5-8.0	10.0-12.8	7.0-9.0	2.0-3.0	2.5-4.0	4.0-6.5	3.5-4.5	7.0-9.0
BOD 5 day at 20°C(Total)	1,100-2,500	5,000-10,000	1,000-3,000	400-700	350-800	800-1,100	1,000-2,000	1,200-3,,000
COD (Total)	3,000-6,000	10,000-25,000	2,500-7,000	1,000-3,000	1,000-2,500	2,000-4,500	2,500-7,000	2,500-8,000
Sulphides (as S)	-	200-500	30-60	-	-	-		30-150
Total Solids (TS)	32,000 – 55,000	24,000-48,000	5,000-12,000	35,000-70,000	30,000-60,000	10,000-14,000	4,000-9,000	12,000-23,000
Total Dissolved Solids (TDS)	30,000-48,000	18,000-30,000	3,000-8,000	34,000-67,000	29,000-57,500	9,000-12,500	3,600-8,000	9,000-18,000
Suspended Solids (SS)	2,000-7,000	6,000-18,000	2,000-4,000	1,000-3,000	1,000-2,500	1,000-1,500	400-900	2000-5000
Chlorides (as Cl)	14,000-28,000	4,000-8,000	1,000-2,000	20,000-30000	15,000-25,000	1,500-2,500	300-1,000	6,000-9,500
Sulphate as SO_4	800-1,500	600-1,200	2,000-4,000	12,000-18,000	13,000-19,000	1,000-2,000	1,200-2,500	1,600-2,500
Total Chromium (as Cr)	-	-	-	-	1,500-4,000	15-30	50-300	120-200

Notes: 1. All values except pH are expressed in mg/l.

2. Volume of wastewater applicable is for hides (cow and buffalo) and goat skins of Asian and African region and not for wool sheep or pig skins.

Table 3. **Average pollution loads in kg in tannery wastewater discharged for one t of hides and/or skins processed from raw to finished leather**

No.	***POLLUTION PARAMETER***	*Soaking operations*	*Beam house operations*	*Tan yard process*	*Post tanning & Wet finishing*	*Total pollution load in kg*
1	Biological Oxygen Demand (BOD), 5 days @ 20°C	12	44	3	12	71
2	Chemical Oxygen Demand (COD)	23	94	10	27	154
3	Sulphides (as S)	-	4	-	-	4
4	Suspended solids	28	65	9	6	108
5.	Total Chromium (as Cr)	-	-	5	1.5	6.5
6	Total Dissolved solids	160	85	130	44	419
7	Chlorides (as Cl)	107	25	54	6	192
8.	Sulphate (as SO_4)	8	9	45	22	84

Note: Refer graphical presentation in *Annexure 3.*

3.1 Sources of Pollution through Pre-tanning (beam house) Operations

3.1.1 Soaking

The starting material for leather processing, in most cases, is raw hide or skin which had been preserved temporarily by the application of common salt at about 40% on raw weight. The common salt, when removed from the skin during soaking operation, constitutes a major source of pollution from tanneries. About 5 to 9 m^3 of wastewater along with 160 kg of salt is discharged from soaking while processing one ton of wet salted hides/skins.

The spent soak liquor is olive green in colour and contains soluble proteins like albumin and has an obnoxious smell. Suspended matters like dirt, dung and blood adhering to the hides and skins are discharged with the soak liquor. The salinity of soak liquor is very high. The TDS content ranges from 30,000 to 48,000 mg/l and the chloride content (as Cl^-) various from 14,000 to 28,000 mg/l.

Since the dissolved sodium chloride is not easily treatable and removed from the wastewater, the discharge of untreated spent soak wastewater into land leads to the significant addition of salinity to the soil. The transport of salt through the ground water affects the water bodies in the region posing a major environmental challenge. Cost effective solutions to the TDS problem through either avoidance or end of pipe treatment are not yet forthcoming.

3.1.2 Sulphide liming

At the pre-tanning stage, significant amount of chemicals are employed mostly as aided chemicals. The removal of hair and flesh from skin is facilitated during the liming operation. Conventional process employs 10% lime (calcium hydroxide) and 2% sodium sulphide on hide/skin weight basis for loosening of hair. About 5 m^3 of spent lime liquor is discharged per ton of raw hides/skins processed. Sodium sulphide being a good reducing agent interferes in the oxidation of organic wastes and contributes significantly to the BOD and COD concentrations in the wastewater. The spent lime liquor is highly alkaline (pH 10-12). The major amount of pollution in terms of BOD (5,000-10,000 mg/l), COD (10,000-25,000 mg/l), sulphide (200-500 mg/l), and suspended solids (6,000-10,000 mg/l) is contributed by sulphide-liming process. This is due to the poor quality of calcium hydroxide and other chemicals used without proper control in the input quantity.

3.1.3 Deliming

Deliming agents based on weak acidic salts like ammonium chloride and ammonium sulphate are employed to neutralize lime after the hair and flesh are removed from skin. About 1.5 m^3 of spent deliming liquor is discharged per ton of pelt processed. Though the BOD&COD contribution are not significant, the TDS contribution in terms of chlorides or sulphates is high depending upon the nature of ammonium salt. It has now been recognized that the use of nitrogen bearing salts could affect the N:P:K ratio of soil. Also in biological treatment ammonium salt affects the nitrification and denitrification process that will be an important factor in future, though currently it is not taken as an important aspect by pollution control authorities in India and other developing countries. Nitrogen based deliming agents are considered a long-term environmental threat.

3.1.4 Bating

Selected tanneries mostly in the processing of skins do bating. Bating is an enzyme based operation in which the selective removal of globular and interfibrillary proteins is achieved. Although the release of such proteins into wastewater could lead to significant BOD and COD loads, at this stage it may be unavoidable. The contributions to BOD and COD loads by the bating formulations could be minimized through careful choice of such materials.

3.1.5 Pickling and tanning

Use of sodium chloride (8%) and sulphuric acid (2%) commonly adapted in pickling operation leads to significant discharge of TDS, chlorides and sulphate in the effluent. The pickle liquor is highly acidic (pH 2 to 3) and contains TDS (34,000 to 67,000 mg/l), chlorides (20000 to 30000 mg/l) and sulphate (12,000 to 18,000 mg/l). In case of vegetable tanning, there is no need for an extensive pickling. Pickling and chrome tanning are two stages in leather processing which need close scrutiny for their contributions to pollution and damage to environment. It has now been established that sulphate ions in wastewater, which is about 60% from the pickling and chrome tanning, constitute a major source of environmental damage.

Sulphate ions undergo ready reduction to sulphide under anaerobic conditions in wastewater ponds, stagnated wastewater in sewer system, anaerobic wastewater treatment systems like in the anaerobic lagoons, contact filter or Upflow Anaerobic Sludge Blanket (UASB) system etc. adopted in few specific tropical countries like India, South Africa etc.

3.3 Sources of Pollution Through Tanning Operations

3.3.1 Vegetable tanning

The wastewater from vegetable tanning process contains highly polluting organic matter since many tanneries use barks and nuts for tanning in pits particularly in South Asian countries and the uptake of vegetable tanning by the leather is less than 50% of the vegetable tanning applied. Vegetable tanning method does not need the prior preparation stage of pickling and therefore the contribution to pollution load from sulphate salts is lower. But these contribute to high BOD (10,000-20,000 mg/l), COD (20,000-35,000 mg/l) and suspended solids (10,000-15,000 mg/l). Further, vegetable tannins are hard biodegradable materials. Therefore, waste bearing vegetable tannins degrade, although slowly.

3.3.2 Chrome tanning

Chrome tanning is another major and commonly employed method for permanent preservation. The wastewater from chrome tanning contains a large amount of chromium since only 50 to 70% chromium applied in the form of basic chromium sulphate (BCS) is taken by leather and the balance is discharged as waste. In this method, spent solutions containing chromium salts as Cr (1,500-4,000 mg/l), chloride (13,000-25,000 mg/l) and sulphate (13,000-19,000 mg/l) are discharged. The contributions to TDS and chromium concentrations raise ecological concerns. Although the oxidation state of chromium in the tanning salt is only trivalent, discharge norms do not often specify the redox states, because of the concerns of possible conversion of the trivalent state to the more toxic hexavalent form. It is estimated that annually 600,000 t of BCS is used by the tanneries through out the world (1998 data) and about 250,000 t of chromium in terms of BCS is discharged as waste in the effluent. This causes difficulties in effluent treatment and sludge disposal. The spent chrome tanning solutions are sources of both TDS and chromium pollution and this problem has to be addressed.

3.4 Sources of Pollution through Post tanning Operations

Sources of pollution from post tanning operations, are mainly from retanning, rechroming, dyeing and fat liquoring.

In the post tanning operations, the tanning industry employs a wide range of performance chemicals which add aesthetic properties to leather. Many of these are formulations based on proprietary products. However, it is now realized that post-tanning processes contribute to neutral salts, mainly sulphate, COD and heavy metal pollution. These apart, azo dyes, biocides and some heavy metal based pigments add to non-biodegradable pollution load of wastewater streams.

The contributions to BOD, suspended solids, chloride loads in wastewater are significantly lower from the post tanning operations in comparison to the total discharge. But the contribution of Chromium (50-300 mg/l), TDS (3,000-5,000 mg/l), sulphate (1,500-2,500 mg/l) and insoluble COD are significant due to the presence of non-biodegradable matter. It is therefore necessary to carry out treatability studies on the proprietary formulations so that non-degradable substances may be avoided.

Since post-tanning operations are associated with size reduction of the leather matrix, a significant amount of solid wastes is generated. Wet-blue shavings, buffing dust and trimmings face constraints in utilization/disposal. Buffing dust and fine particulate matters can be air borne and emerge as a source of air pollution. Solvent based finish formulations employed in leather processing increase the potential for atmospheric pollution. *Formaldehyde used in leather finishing has been a disconcerting source of pollution.*

4. ESTIMATION OF POLLUTION DISCHARGE

The quantum of pollutional discharge varies from process to process and tannery to tannery. Some of the operations, though found to be common, may still produce wastewater of varying concentrations. Hence sampling and analysis from sectional discharge, composited waste at least 3 different set and season is considered necessary to get a fairly realistic average value. In addition to estimation of total BOD and COD, the corresponding soluble BOD and COD should also be estimated in order to formulate suitable physical-chemical and biological treatment systems. A typical example of total and soluble BOD & COD of the composited tannery wastewater from different tanning operations is given in *Table 4.*

Table 4. **Soluble BOD and COD of composite wastewater from various tanning processes**

No.	Type of process	BOD			COD		
		Total mg/l	*Soluble mg/l*	*Soluble %*	*Total mg/l*	*Soluble mg/l*	*Soluble %*
1.	Raw to E.I	2,780	2,225	80	5,700	4,275	75
2.	Raw to wet blue	2,300	1,725	75	4,660	2,140	46
3.	Raw to finish	1,700	1,200	70	3,570	1,600	45
4.	Wet blue to finish	1,010	830	82	2,210	1,600	72
5.	E.I to finish	1,060	850	80	3,930	2,900	74

The pollution concentration in terms of BOD, COD, TDS, chloride, etc., is comparatively high in some region like South India, Italy etc., since the volume of water used per ton of raw material processed is low (about 30 m^3/t) when compared to tanneries in North India (Calcutta), Bangladesh, China, Egypt etc. where they use 40 to 70 m^3 of water per ton of raw material processed. Hence for the estimation of pollution load both the volume of discharge and pollution load per ton of raw material processed need to be taken into account.

Nearly 50% of the total dissolved solids (TDS) and more than 60% of the chlorides are contributed by spent soak wastewater mainly due to the use of common salt for curing of hides and skins. Few tanneries located mainly near cities and having organized slaughterhouse process fresh hides and skins without the application of salt for curing.

More than 60% of BOD and COD are contributed from lime sulphide, fleshing and deliming operations. The concentration of suspended solids in spent lime liquor is very high and ranges from 8,000-20,000 mg/l. This is mainly due to the poor quality of calcium hydroxide and other chemicals used in excess quantity due to lack of proper control in beamhouse operations.

More than 90% of sulphide is discharged from the spent lime liquor and wastewater from mechanical fleshing operation. This sulphide concentration increases the COD load and when it is oxidized it will be converted into sulphate and increases the TDS and sulphate concentration in the final treated effluent.

About 60% of the sulphate is discharged from pickling and chrome tanning operations. This is mainly due to the use of salt and sulphuric acid in pickling and wastage of more than 40% basic chromium sulphate used in chrome tanning operation. About 30% of sulphate is discharged from retanning, rechroming, and wet finishing operations. In addition to high sulfate major part of the non-bio degradable COD is generated in the post tanning operations. This is mainly due to the use of, syntan, fat liquors and other sulphonated components in the finishing operations.

The increase in sulphate not only increases the TDS in the effluent but also causes corrosion and affects the anaerobic biological treatment process. For efficient anaerobic process the sulphate concentration shall be preferably less than 25% of the degradable COD value in the composited tannery effluent.

Periodical analysis of the sectional and composite waste streams and quantitative estimation of the pollutional discharges are considered necessary. It will also be helpful in formulating suitable mechanism in cost sharing by the tanners in the operation and maintenance of the CETPs based on pollutional discharge.

5. INTERNATIONAL SCENARIO ON ENVIRONMENTAL REGULATIONS

5.1 General

Environmental regulations and laws in many developing countries have been passed mostly during the last decade but the compliance has not always been practical, either because the laws either too ambitious or unrealistic in case of certain parameters, or because they have lacked effective instrumentation and institutional support. Some environmental laws have not succeeded as they do not match the technical requirements and economic reality of the country or region, or because they do not take the institutional capabilities of the society that has to implement them into consideration.

The basic working paper compiled by UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION (UNIDO), Vienna entitled "Pollution limits for discharge of effluents into water bodies and sewers" from 46 countries covering Argentina, Australia, Austria, Brazil, China, Colombia, Costa Rica, Croatia, Czech Republic, Denmark, Egypt, Finland, France, Germany, Greece, Hungary, India, Indonesia, Iran, Ireland, Italy, Japan, Kenya, Mexico, Netherlands, New Zealand, Nicaragua, Pakistan, Philippines, Poland, South Africa, Spain, Sri Lanka, Switzerland, Tanzania, Thailand, Tunisia, Turkey, Uganda, UK, Uruguay, USA, Venezuela, Vietnam, Zambia and Zimbabwe has been updated and given as *Annexure 2*.

5.2 Environmental Standards

The salient parameters adopted for limits for the discharge of tannery effluents by more than 90% countries are; pH, temperature, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), total solids, settleable solids, total chromium and sulphides. Few countries like India and Egypt included the parameters for Total Dissolved Solids (TDS). The definitions of salient pollution parameters adopted and the procedure for their estimation are given in *Annexure 1*.

Most of the countries are having two standards; one for discharge into water bodies and other for discharge into sewerage system. In few developed countries discharges are to sewerage systems where there may be comprehensive treatment before return to the environment via surface waters. In these cases, standards set by the authorities treating the effluent are dependent on the dilution with other effluents and domestic sewage, the capabilities of the treatment plant, and problems that might be experienced in the management or maintenance of the plant and equipment. The limits to discharge in to sewage system are thus lower than when discharge is to surface waters. However, factors such as the disposal of final sludge, and discharge limits for the treated effluent that might be imposed on the sewage treatment authority also have to be taken into account.

Where effluent discharge is directly into streams and rivers, the effluent needs to be of higher quality, as the environment is sensitive and readily damaged. The greater the volume of the effluent compared to the volume of surface water, then the higher the quality of the effluent demanded by the environment.

Discharge limits are set with the objective of protecting the environment, and there are two basic ways that determine the levels of the different effluent components.

(i) Based on data that has been applied and found generally acceptable in a wide range of global situations. This method is adopted in most of the developing countries but does not tend to take into account individual situations.

(ii) Situations when a mass-balance is applied. In this method the quality of the water upstream is determined, and the quality requirements of the water downstream, i.e. for industry or potable use. The difference between the two figures is determined, and this sets the tolerance levels at the point of discharge.

The second technique takes into account individual site factors and considered to be most realistic and applied in limited number of countries.

The list of values are often required by the environmental protection agencies are usually expressed in milligrams/litre (mg/l) sometimes as parts per million (ppm). The limits imposed should always relate to the volume of effluent to account for the total weight of pollutants. If better housekeeping reduces the volume of water used, thus increasing the concentration, then there is good reason for some relaxation of the limits.

Often limits and guidelines do not reflect the individual situation, but there is a need to protect the environment from overload. The effect of excessive constituent levels commonly found in tannery effluents can be severe and is presented for guidance.

6. POLLUTION CONTROL REQUIREMENTS AND EFFLUENT MANAGEMENT

In most of the developing countries according to the environmental pollution control regulations, the tanneries are obliged to set up effluent treatment systems either individually or collectively and the treated effluent shall meet the relevant pollution control standards.

A typical example on the salient parameters of the raw untreated composited effluent and the expected level of treated effluent for discharge into inland surface water is given in *Table 5.*

Table 5. **Typical composite untreated tannery effluent, Indian standard for discharge of effluent into surface water and corresponding expected percentage of removal**

Parameter		*Unit*	*Chrome tannery raw mixed effluent range (average)*	*Permissible limit discharge into surface water*	*Expected percentage removal*
1.	pH		6-9	6-9	--
2.	Temperature	°C	20-35	20-35	--
3.	BOD_5	mg/l	2,000	30	98.5
4.	COD	mg/l	5,000	250	95
5.	TSS (ash)	mg/l	4,000	100	97.5
6.	TDS (ash)	mg/l	8,000	2,100	74
7.	Oil and Grease	mg/l	150	10	93
8.	Sulphates as SO_4	mg/l	2,000	1,000	50
9.	Chlorides as Cl	mg/l	4,000	1,000	75
10.	Total Chrome as Cr	mg/l	150	2	98.5
11.	Sulphides as SO_2	mg/l	200	2	99

The tanneries in many developing countries can be grouped into four major categories for effluent treatment and management.

1. Large and medium scale tanneries with adequate land, finance and managerial capacity had to set up individual effluent treatment plants.
2. Tanneries located in clusters and do not have adequate land and financial/technical capability to set up individual effluent treatment units but feasible to set up CETP had to provide CETP system.
3. Cluster of tanneries in cities like in Istanbul and Izmir in Turkey, Calcutta, Jalandhar and Bombay in India, Colombo in Sri Lanka, Cairo in Egypt etc where there is no scope even for a CETP due to non-availability of adequate land, public resistance from the surrounding area, other socio-economic aspects etc. had to relocate and develop separate industrial complex with CETP system.
4. Scattered small-scale tanneries, which neither can set up individual effluent treatment plant nor be included in a planned CET system, had to relocate and join one of the clusters with CETP system or to close down.

Treatment technologies adopted generally in tropical conditions comprises of four steps namely:

- *(i)* segregation of certain sectional waste streams like soak liquor, chrome liquor etc or mixing of suitable sectional wastewater from different process and cleaner technologies like chrome recovery and reuse etc.;
- *(ii)* primary treatment in individual tanneries or in a centrally place wherever a CETP is established;
- *(iii)* secondary biological anaerobic/aerobic treatment and
- *(iv)* disposal of sludge from effluent treatment plants.

Tannery effluent treatment systems popularly adopted in developing countries are shown in *Annexure 3.*

6.1. Segregation of streams and pre-treatment in tanneries

In South Indian tanneries the salt laden effluent from the soaking operation is collected separately in the open impervious shallow evaporation pans of depth 20 to 30 cm and allowed to evaporate using solar energy. To reduce the suspended and colloidal impurities physical-chemical treatment is required before discharge of soak liquor into solar evaporation pans. The evaporation rate varies from 100 to 250 cm per year depending upon the characteristics of wastewater and local atmosphere conditions like temperature, humidity, wind velocity, rainfall, etc. For operational reasons, the solar evaporation pans are divided into four or more compartments. The dried salt is manually scrapped, collected and advised to be dumped into sea, wherever possible, or reused after purification along with fresh salt for preservation of raw hides and skins and for pickling operation.

The segregation of soak liquor and evaporation in solar pans may not be feasible in cold regions and where monsoon is severe. Other treatment methods for the treatment of soak wastewater like Reverse Osmosis (RO), desalination etc., could also be considered, but the complicated physical-chemical and treatment steps required to make the soak waste water fit for RO, the capital and operational costs of the treatment system will be very high and not feasible for field implementation in all locations.

The following segregation of wastes and separate treatment of certain streams are also adopted in some tanneries.

- *(i)* The sulfide liming effluent is collected and treated separately by aeration with diffused air or other type of aerators in the presence of catalyst like manganous salt to reduce sulfide before mixing with other wastewater.
- *(ii)* The exhaust chrome liquor is collected separately for recovery and reuse of chromium. Full scale demonstration chrome recovery systems implemented under UNIDO assisted programme in a tannery cluster near Madras in India and Birgunj in Nepal, Colombo in Sri Lanka are found viable for small and medium scale tanneries processing up to wet-blue. Based on the success of these demonstration units many tanneries have willingly started adopting the system. Chrome recovery and reuse is now popular and mandatory in most of the developing and developed countries.
- *(iii)* Many other cleaner technologies like sulfide reduced liming, carbon dioxide deliming, high exhaustion of chromium and other recirculation techniques are followed in few tanneries particularly the units processing skins and facility for lime splitting of hides.
- *(iv)* Simple screen chamber with fixed or rotary screens is necessary before discharging the effluent to the pipeline or channel leading to the effluent treatment plant.

6.2. Primary (physical-chemical) treatment units

Primary treatment is necessary to remove coarse and floating particles of bigger size, equalize or neutralize various streams of different pH and characteristics, removal of major part of suspended solids (80-90%), chromium (95-99%), sulfides (90-95%) and make the effluent of uniform quality, reduced pollution load and fit for secondary biological treatment.

The primary treatment units principally comprise of fixed and/or mechanical screens equalization cum mixing, chemical dosing system and primary settling. Depending on the quality of composite effluent, chemicals like lime, alum, polyelectrolyte etc are added for effective precipitation and removal of suspended solids in the sedimentation process in hopper bottom settling tank or clarifier with detention time of 3 to 4 hours. Special techniques like dissolved air floatation have been adopted in some of the ETPs in India in place of primary and secondary settling tanks.

In many tropical countries with low rainfall and locations where large land space is available, the sludge is dewatered and dried on sludge drying beds. The sludge drying beds are made up of filtering media like gravel, sand and supporting masonry structure. The sludge-drying period varies from 8 to 15 days depending upon the type of sludge, atmospheric conditions etc. The dried sludge from sludge drying beds contains moisture of 40 to 60%. Mechanical dewatering units like belt press, centrifuge and pressure filter are also used in effluent treatment plants particularly in cold countries and places where land is also not available. Dewatered sludge is used as manure or for landfill if it is a vegetable tannery waste. In case of chrome tannery waste, the dried sludge needs to be disposed off suitably as per the directions of regulatory agencies and local bodies. The disposal of chrome containing sludge is one of the serious problems in India like in any other country of the region.

6.3. Secondary biological treatment units

Primary treatment system removes major part of suspended solids, sulphide chromium, BOD and COD corresponding to the suspended/settleable matter. 40-60% of the total BOD/COD is contributed by soluble organic and unsettled colloidal matter and can be removed only by biological treatment.

After primary treatment two stage aerobic biological treatment units generally adopted in most of the countries in Europe, America etc. In few selected countries like in India, South Africa etc anaerobic systems like anaerobic lagoons followed by aerobic pondings and or extended aeration system are adopted in addition to aerobic systems. Salient Combinations are:

(i) Anaerobic lagoon followed by aerated lagoon or activated sludge process or extended aeration

(ii) Aerated lagoon followed by extended aeration system or two stage extended aeration system are commonly adopted in most of the developed and developing countries.

(iii) Upflow Anaerobic Sludge Blanket (UASB) system followed by aerobic treatment system has been implemented in one of the CETPs in India for combined treatment of domestic sewage and tannery effluent.

7. EXPERIENCES IN COMPLIANCE OF REGULATIONS AND IN SETTING UP OF TREATMENT PLANTS

7.1 Treatment Plant Capacities

The volume of wastewater discharge and characteristics vary from process to process and tannery to tannery. Hence, detailed inventory and survey of the tanneries including their future plan are required before designing every plant. Most of the effluent treatment plants particularly CET plants in India and Turkey are either under utilized or under designed.

7.2 Design of Treatment Plants

Most of the consultancy firms in developing countries have experience only with the design and execution of laying sewer and treatment system for domestic wastewater. As the tannery effluent is complex in nature, variable in quality and quantity, knowledge and experience in the tanning process, effluent characteristics, treatment technology and operation and maintenance would be necessary for the design of the treatment system.

7.3 Sectional of Site and Appropriate Treatment Technology

For selection of treatment plant site and treatment technology, study on techno-economic aspects including topography, capital investment, final mode of treated effluent, operation and maintenance cost, land requirement, availability of skilled manpower, influence of the treatment cost on the production of leather etc. are necessary.

7.4 Cost Estimate and Financing

The capital cost of an effluent treatment plant depends upon the type of treatment technology, location, final mode of disposal etc. Capital cost for implementing 1000 cubic meter/day capacity effluent treatment plant would range from US$ 0.6 to 1.0 million as per 1998 rates. Treatment cost of 1,000 cubic meter effluent including operation and maintenance cost, financial cost etc. would range from US$ 300 to 750 or equivalent to US$ 0.8 to 2.0 for producing 100 sq.ft of finished leather. But this cost estimate for the effluent plants are made on capital investment of the plants and annual operation and maintenance for utilization of its designed capacity without provision for escalation, repayment of loan, depreciation, time and cost involved in initial standardization of the process, actual percentage utilization of the plant, sludge disposal etc. In view of this most of the projects cost estimates have become unrealistic and ended with revisions.

7.5 Equipment & Materials of Construction

Selection of suitable equipment and materials for construction is an important factor. Though most of the mechanical and electrical items for the setting up of effluent plants are manufactured in many developing countries, few items need improved design and quality in view of the special requirements in the treatment of tannery effluent. Some of the identified items are:

(i) special mechanical rotary screens/sieve arrangements,
(ii) mechanical sludge dewatering systems,
(iii) efficient trouble free aeration systems for biological treatment.

Due to unsuitable selection of equipment like conventional miled bar screens, aerators without proper design etc the desired performance efficiencies could not be achieved in some of the treatment plants.

7.6 Operation and Maintenance of Effluent treatment system

The important problems faced in the, operation and maintenance effluent treatment systems are:

- Major seasonal variations in the production capacity and effluent discharge which results in under utilization or over loading of the treatment system.
- Few tanneries totally modify the process after implementation of the effluent treatment system (i.e. from vegetable tanning to chrome tanning, processing from wet blue to finishing instead of raw to finishing and vice versa) and resulted in major change in the quality and quantity of effluent and maintenance of effluent treatment plant.
- Use of toxic and excess non-biodegradable chemicals, preservatives and other inorganic chemicals supplied under commercial name, often vary the quality of effluent and affect the biological treatment systems.
- Discharge of solid waste like fleshings, vegetable tan barks, leather pieces in the wastewater drain leading to effluent treatment plant without proper control.
- Choking and overflowing of the sewer are common occurrences. These are due to poor pre-treatment arrangements in the individual tanneries and in some cases, the design of drainage system was not properly done considering the peak flows and other variations.
- Mixing of rainwater with tannery effluent often cause over loading of treatment units in the absence of by-pass arrangements.
- Non-segregation of certain specified streams like soak liquor, pickle liquor, chrome liquor etc from the main waste stream which are originally designed for separate treatment.
- Insufficient nutrient supply, improper maintenance in recirculation of active sludge and control of MLSS in the extended aeration/activated sludge processes often affects performance efficiency.
- Operation and maintenance of the treatment units with unskilled manpower who has no knowledge and experience in the tannery effluent system
- Supply of uninterrupted power supply to the effluent treatment plants is one of the main constraints. Though few CET plants are having alternative power supply arrangement using diesel generators, providing continuous power is often faced with problems when main power supply breaks down for a long period of more than 4 to 6 hours. In addition, the energy supplied from diesel generators is costly.
- Disposal of chrome containing sludge, which accumulates in large quantities in the effluent treatment plant area, is another major problem in the absence of proper utilization/disposal

methods. Legislation and standards is not existing in most of the developing countries for the disposal of sludge.

- Constraints in the sharing of cost towards the operation and maintenance of CET plants by the tanneries in the absence of suitable and acceptable formula.
- The conventional physical-chemical treatment systems adopted are expected to reduce or remove suspended solids, BOD, COD, Sulfide, Chromium etc and not TDS and Chloride. In view of this the pollution control parameters like TDS (less than 2100 mg/l), Chlorides (less than 1000 mg/l), COD (less than 250 mg/l) etc insisted by few countries like India and Egypt are very difficult to achieve in spite of segregation and disposal of saline streams from soaking, pickling and chrome tanning.

8. VIEWS AND SUGGESTIONS

Tannery effluent is complex in nature. The characteristic of pollution discharge varies from process to process and tannery to tannery. Most of the tannery effluent treatment plants particularly CETPs are either under designed or under utilized and not able to comply with the environmental regulations of the country. The tanners are mostly conservative in nature and they believe what they see and do not disclose what they do. Some of the cleaner technologies which provide direct financial benefit like chrome recovery and reuse are adopted successfully by many units, the other cleaner technologies which are not shown much direct benefit are yet to become popular. Programmes for demonstration and wide dissemination are considered necessary. Organized inventory, survey, characterisation of the pollution discharged from the tanneries, proper planning, techno-economic feasibility study of the effluent treatment systems, in-process control, continued monitoring of treatment systems, training and demonstration are necessary not only for tanners and technical staff in the operation and maintenance but also to the environmental pollution control agencies in association with organizations like UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION (UNIDO), leather and environmental research organisations having experience in tannery waste management programme are considered necessary for the sustainable development of the leather tanning industry.

POLLUTION PARAMETERS OF TANNERY EFFLUENT AND THEIR ESTIMATION

1. Solids

There are several different classes of solids found in tannery effluent.

1.1. Suspended solids (SS)

The suspended solids component of an effluent is the quantity of insoluble matter contained in the wastewater. These insoluble materials cause a variety of problems when they are discharged from a site, and essentially are made up of solids with two different characteristics.

a. Solids with a rapid settling rate

This is material which can be seen in suspension when an effluent sample is shaken, but settles out when the sample is allowed to stand. The majority of these solids settle out within 5 to 10 minutes, although some settling of fine solids can still be taking place after 1 hour.

These solids are produced from all parts of leather making and are comprised of fine leather particles, residues from various chemical discharges and products from different waste liquors reacting together. A very large quantity is generated from beamhouse processes.

If the wastewater are for treatment as provided by sewage works or common effluent treatment, the main problems are due to the considerable volume of the sludge formed as the solids settle out. Sludge often contains up to 97% water creating huge quantities of 'light' sludge. Even viscous sludge contains water at around 93%, and can easily cause blockages in sumps, sludge pumps and pipe work. All of this sludge has to be removed, transported, dewatered, dried and deposited causing high demands on plant, equipment and resources.

If the discharge is into surface water, then the flow rate will strongly influence how far the material carries before it settles out on the bed of the stream or river.

Even a thin layer of settled sludge can form a blanket that cuts off oxygen from that area of the river or lakebed. The plant and aquatic life die creating foul conditions.

b. Semi-colloidal solids

These are very fine solids that for practical purposes will not settle out from an effluent sample, even after standing for a considerable time. They can, however, be filtered from solution and therefore, together with the more readily settleable solids, form the suspended solids of an effluent as measured analytically.

The majority of these solids are protein residues from the beamhouse operations – mainly liming processes – but high quantities are also produced from poor uptake in vegetable tanning processes. Other sources are from poor uptake in retanning areas.

These solids will not directly cause sludge problem, but they can break down in the long term. This is by bacterial digestion producing solids that will eventually settle, and also a high oxygen requirement. This oxygen demand is considered in Section 3.2.

The suspended solids analysis measures both of these components and the technique is simple. A known volume of the effluent is taken and filtered through a filter paper, which is then dried and reweighed. The difference between this weight and that of the original paper is the weight of the dry solid material contained in the sample.

1.2. Settleable solids

Although the suspended solids analysis is the most common method used to assess insoluble matter, sometimes the settleable solids content is required. This measures the solids component with the fast settling rate. This can be determined by allowing the shaken sample to settle and filtering a known volume of the semi-colloidal matter remaining in suspension. After drying and weighing, the quantity of semi-colloidal matter can be calculated. The difference between the suspended solids and this figure is the level of settleable solids.

1.3. Gross solids

These solids are larger than a sampling machine can handle and are therefore not measured. Their presence is, however, obvious and fully recognized due to the dangers that they present.

The waste components that generate this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and frequently broken down paper from bags. They can be removed easily by coarse bar screens set in the wastewater flow, but if they pass from the factory they settle out very rapidly.

Major problems can develop with these materials if they settle in pipe work as they provide a source of blockage. The problem can become very serious when effluents have to be pumped as often the blockages occur in inaccessible pipe work. The cost of replacing a burned out motor or broken rotors is high.

If discharged into gullies, ditches or watercourses the debris rapidly accumulates causing blockage and stagnation.

2. Oxygen demand

Many components in effluents are broken down by bacterial action into more simple components. Oxygen is required both for the survival of these bacteria (aerobic bacteria) and for the breakdown of the components. This breakdown can occur quite rapidly or may take a very long time according to composition.

If the effluent creates a high oxygen demand and is discharged directly into surface water then the sensitive balance maintained in the water is overloaded. Oxygen is stripped from the water causing oxygen dependent plants, bacteria, fish and the river to die. An environment where bacteria which are non-oxygen dependent (anaerobic) then becomes established creating toxic conditions in the waterway.

A healthy river can tolerate low levels of oxygen demanding substances, but the load created by tanneries is often very high, and the effluent requires treatment before discharge. This is often provided by using bacteria in a properly operated effluent treatment plant and high levels of oxygen are demanded by the process. This oxygen can be induced into the effluent by blowing in large volumes of air, but this requires a high level of energy. The plant has high capital and operational costs.

If the process works ideally, then water and carbon dioxide are produced in large volumes, but the process depends upon the growth of bacteria. As these die they form a sludge that has to be treated and ultimately disposed. This sludge has high water content and is often quite difficult to dewater adding considerably to the treatment costs.

To assess the impact of an effluent on either discharge to surface waters or to set a value on the costs of treatment, the oxygen demand needs determining and this can be achieved in two different ways.

2.1. Biochemical Oxygen Demand (BOD_5)

The technique for measuring the Biochemical Oxygen Demand (BOD) is complex. Essentially, the shaken effluent sample is allowed to stand for one hour so that all settleable solids are excluded from the analysis. The liquor (supernatant) above the precipitate is drawn off and used in the analysis. A suitable volume of this sample is diluted in water, pH adjusted, and seeded with bacteria (often-settled sewage effluent). The samples are then incubated for 5 days in the dark at 20 ± 1°C. Oxygen dissolved in the water is used by the bacteria as the organic matter in the sample is broken down. The remaining oxygen is determined either by an oxygen meter or by analysis. By comparison to effluent free blank samples, the level of oxygen demanded by the effluent can be calculated.

The BOD_5 analysis, generally termed BOD, is widely used to assess the environmental demands of a wastewater. There are various weaknesses with this method of detection: the bacterial cultures can vary and the analysis is sensitive. If the most stringent care is not taken in preparation and analysis the results can be misleading.

It should also be remembered that although this is a measure of the oxygen requirements of bacteria under controlled conditions, many effluents components take longer than this time to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period often quoted up to 20 days. These longer digestion periods can apply to a variety of the chemicals used in manufacturing leathers including certain retanning agents, some synthetic fat liquors, dyes and some residual proteins from hair solubilization.

This longer breakdown period spreads the environmental impact to a greater area, as the wastewater components are carried greater distances before breakdown.

2.2. Chemical Oxygen Demand (COD)

This method measures the oxygen required to totally oxidize the effluent sample. It sets a value on the materials that would normally be digested in the BOD_5 analysis, the longer-term biodegradable products, and also chemicals that are not affected by bacterial activity.

The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidizing agent (potassium dichromate) and sulphuric acid. As the effluent components oxidize they remove oxygen from the potassium dichromate and this removal is determined by titration.

This method is often favored as it provides rapid results (hours as opposed to days). It is more reliable and cost effective, as it is easier to manage larger numbers of samples.

These results are always higher than the BOD_5 results. As a rule of thumb the ratio between COD:BOD is 2.5:1, although variation can be found in untreated effluent samples as great as 2:1 and 3:1. This is dependent upon the chemicals used in the different leather making process and their rate of biodegradability.

It should be noted that both of these techniques are based on settled effluent, not filtered. 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.

2.3. Permanganate value (PV 4 hours)

This technique is occasionally used and depends upon chemical oxidation provided by potassium permanganate. Determination by COD has almost completely replaced this method.

3. Nitrogen

Nitrogen is contained in several different components in tannery effluent and sometimes there is a need to differentiate between these sources.

3.1. Total Kjeldahl Nitrogen (TKN)

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia from deliming materials, and the nitrogen content of proteinaceous materials resulting from liming/unhairing operations.

There are two direct problems resulting from these sources of nitrogen.

1. Nitrogen is required for plant growth, but high levels made available from nitrogen containing substances overstimulate this development. Water based plants and algae grow too rapidly, so waterways become clogged and the flow can become restricted. As these plants die, there is a disproportionately high amount of organic matter for breakdown. If the natural supply of oxygen from the river is exceeded by this load, then plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop.
2. Nitrogen released from the breakdown of proteins and from the deliming process exists in the ammoniacal form. This can be converted by bacteria through several stages to form water and nitrogen gas that is released to the atmosphere. Both of these breakdown products are non-toxic, but large quantities of oxygen are needed in the process. If this oxygen demand is greater than the natural level of supply in a watercourse, then toxic anaerobic conditions rapidly develop.

These nitrogen containing compounds can be broken down by biological effluent treatment in a similar way to treating effluents to reduce the BOD. The oxygen demand is very high – hence plant size and energy costs – and calculations show that with a typical tannery effluent, around 40% of the oxygen requirements are taken up by removing the nitrogen component.

The nitrogen containing compounds can be determined by the Kjeldahl method of analysis. In this technique, all the nitrogen containing matter is digested by boiling with sulphuric acid to form ammonium compounds. In a second stage this ammonia is released by boiling with sodium hydroxide, then trapped in boric acid solution. The level of ammonia released is determined by titration and the value as nitrogen calculated.

3.2. Ammonium content as Nitrogen (N)

This is sometimes required in discharge limits and often confused with TKN. As ammonium compounds are part of the TKN the problems associated with rapid plant growth and oxygen demand are the same. These compounds mostly result from the deliming process, with a comparatively small quantity produced from liming and unhairing. The analysis is similar to TKN but omits the initial digestion stage. This excludes the nitrogen component resulting from protein wastes.

4. Sulphide (S^{2-})

The sulphide content of a tannery effluent results from the use of sodium sulphide and sodium hydrosulphide, and the breakdown of hair in the unhairing process.

There are many problems associated with this material:

- Under alkali conditions sulphides largely remain in solution. When the pH of the effluent falls below 9.5, hydrogen sulphide is evolved from the effluent – the lower the pH, the greater the rate of evolution. Characterized by its smell of rotten eggs a severe odor problem is created.
- This gas is as toxic as hydrogen cyanide and even low-level exposure will cause headaches and nausea, and there is a danger of attack to the surface of the eye. At higher levels death can rapidly result and there are many deaths recorded from sulphide build up in sewage systems.
- Hydrogen sulphide gas is also fairly soluble, and when dissolved by condensation weak acids can be formed with resultant corrosion. This typically weakens metal roofing, girders and metal building supports. In sewers major problems can result by corrosion of metal fitting, re-enforcement and pipe work.
- If discharged to surface water, there are toxicological dangers even at low concentrations. Sulphides can also be oxidized into non-toxic compounds by certain bacteria in rivers, but this creates an oxygen demand and if excessive there is damage to aquatic life.

There are several methods of determining sulphides in effluent. One of the most accurate relies on the acidification of suitable quantities of effluent to generate hydrogen sulphide. This is flushed through the apparatus using nitrogen gas, trapped and converted into zinc sulphide. The level of sulphide is determined by titration.

5. Total Dissolved Solids (TDS) and Neutral salts

5.1. Total Dissolved Solids (TDS)

The total dissolved solids (TDS) in tannery effluent is mainly contributed by chlorides 940-50%) and sulphates (20-30%).

TDS analysis: A well mixed known volume of sample is filtered through a standard glass fibre filter and filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids (TDS).

5.2. Sulphates (SO_4^{2-})

Sulphates are a component of tannery effluent, having been introduced either by the use of sulphuric acid, or through using products with a high sodium sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-product of their manufacture. For example, chrome-tanning powders contain high levels of sodium sulphate and also many synthetic-retanning agents.

An additional source is created by removing the sulphide component from effluent by aeration as the oxidation process creates a whole range of products including sodium sulphate. These sulphates can be precipitated by calcium containing compounds, forming calcium sulphate which has a low level of solubility. Problems are associated with soluble sulphates, however, for two main reasons:

1. Complete chemical removal of sulphates from solution is not viable. Under certain biological conditions, it is possible to remove the sulphate from solution and bind the sulphur into microorganisms. Generally, however, the sulphate either remains as sulphate, or is broken down by anaerobic bacteria to produce hydrogen sulphide and odour. This process occurs very rapidly in effluent treatment plants, sewage systems and watercourses if effluents remain static. This bacterial conversion to hydrogen sulphide in sewage systems results in corrosion of metal parts, and gradual erosion of concrete will take place unless the concrete is sulphate resistant.
2. If breakdown does not occur, then there is the risk of increasing the total salt concentration in surface waters and ground water.

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

5.3. Chlorides (Cl^-)

Chloride as sodium chloride is introduced into tannery effluents usually from the large quantities of common salt used in hide and skin preservation and from the pickling process. As they are very soluble and stable, they remain unchanged by effluent treatment and nature and remain in the environment. Considerable quantities of salt are produced by industry, and levels can rapidly rise to the maximum acceptable for potable water. Increasing salinity in ground water, especially in areas of high industrial population is now becoming a serious environmental problem.

Inhibition of growth is experienced with plants, bacteria and fish in surface waters, and at high levels can lead to breakdown of cell structure. If the water is used for irrigation, the salt content increases at surface level due to evaporation and crop yields fall. When flushed from the soil by rainfall, chlorides re-enter the eco-system and may enter the ground water. Only if discharges are into tidal/marine environments are high salt contents acceptable.

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

Under neutral or alkali conditions, an excessive addition of silver nitrate is made. This excess is then determined by back titration with potassium thiocyanate using ferric alum as the indicator.

6. Oils and grease

Natural oils and greases are released from within the skin structure during leather manufacture. There may also be some fatty substances produced from inter-reactions when waste waters mix if fatliquor exhaustion is poor.

As greases and fatty precipitates float, they can form mats that collect and bind other materials causing a potential blockage problem especially with effluent treatment systems.

If these fatty substances are in the form of an emulsion, being biodegradable they create a very high oxygen demand.

These components are determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the effluent. This solvent dissolves fatty matter and a quantity can be drawn off and evaporated to dryness. This leaves residual grease for weighing and calculation.

7. pH value

Acceptable limits for the discharge of wastewater to both surface waters and sewers are found from ranging between pH 5.5 to 10.0. Although tighter limits are often set, there is always greater tolerance to the alkali side. This is because carbon dioxide from the atmosphere and from biological processes in healthy surface water systems tends to lower pHs very effectively to neutral conditions. If the pH of surface waters is moved too far either way from the pH range 6.5-7.5, then there is loss of more sensitive fish and plant life.

Municipal and common treatment plants prefer discharges to be more on the alkali side as the corrosive effect on concrete is reduced. Metals tend to remain insoluble and more inert, and any evolution of hydrogen sulphide is minimized. When biological conditions are carried out as part of treatment the pH is lowered to more neutral conditions by evolved carbon dioxide.

8. Chromium compounds

As metal compounds are not biodegradable and can be viewed as remaining long term in the environment, or being accumulative, these receive close attention. There are two forms of chrome associated with the tanning industry, and their properties are often confused.

8.1 Chrome 3^+ (trivalent chrome, chrome III)

Chromium is mainly produced as waste from the chrome tanning process, as part of re-tanning systems and by displacement from leathers by re-tanning and dyeing processes.

This chrome is discharged from processes in the soluble form but when it is mixed with other tannery wastewater from other processes, especially if proteins are present, there is a very rapid reaction. Precipitates are formed, mainly protein-chrome, which add to the sludge generation.

However, very fine colloids are also formed as discussed in Section 1.1.b and these have been made very stable by the chrome – in effect the protein has been partially tanned. This makes this component more resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

When these fine solids are successfully broken down, there will be a precipitate as chromium hydroxide formed which will remain long term in the eco-system.

If chrome discharges are excessive there is the possibility of chromium remaining in solution. In this state it is toxic at low concentrations to daphnia thus affecting the fish food chain, and it can also inhibit photosynthesis.

There are several methods of determination, but the first stage 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. Iodine/thiosulphate titrations are sometimes used where high levels of chrome are expected, but this technique is not accurate at low concentrations.

8.2. Chrome 6^+ (hexavalent chrome, chrome VI)

The presence of chromium in this form is unlikely in tannery effluents unless dichromates are being used as part of chrome manufacture. Dichromates are toxic to fish life, as there is easy penetration of cell walls. Absorption is mainly through the gills and it is accumulative.

Analysis is specialized as concentrations normally anticipated are very low and are based on calorimetric measurement at 670 nm.

9. Other metals

Other metals which might be discharged from tanneries and where limits to discharge may be set include aluminum and zirconium.

These metals have different toxicities according to the chemical species, also by the presence of other organic matter, complexing agents and the pH of the water. In particular, aluminum appears to inhibit the growth of green alga and crustaceans, as they are sensitive to low concentrations.

Cadmium, sometimes used in yellow pigments and is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If it becomes a component of potable water it can cause bone embrittlement.

10. Solvents

The sources of solvents are degreasing and finishing operations. Solvents in effluents discharged to surface waters can form a microfilm on the surface of the waters inhibiting uptake of oxygen. The breakdown of solvents is variable. Some inhibit bacterial activity and remain in the ecosystem for long periods of time. Analysis is highly specialized.

11. Phenol

Phenols, defined as hydroxyl derivatives of benzene and its condensed nuclei, may occur in tannery wastewater as polyphenol mainly due to the use of vegetable tannin in the process. Chlorination of such waters may produce odorous and objectionable-tasting chlorophenols. Part of the phenolic waste is biodegradable and the non-biodegradable part can be removed by chemical oxidation process.

The Chloroform Extraction Method

a. Principle
Steam-distillable phenols react with 4-aminoantipyrine at pH 7.9±0.1 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is extracted from aqueous solution with $CHCl_3$ and the absorbency is measured at 460 nm. This method covers the phenol concentration range from 1.0 mg/l to over 250 mg/l with a sensitivity of 1 mg/l.

b. Interference
All interferences are eliminated or reduced to a minimum if the sample is preserved, stored, and distilled in accordance with the foregoing instruction.

c. Minimum detectable quantity
The minimum detectable quantity for clean samples containing no interferences is 0.5 mg phenol when a 25 ml $CHCl_3$ extraction with a 5-cm cell or a 50 ml $CHCl_3$ extraction with a 10-cm cell is used in the photometric measurement. This quantity is equivalent to 1 mg phenol/l in 500 ml distillate.

d. Apparatus
- i. Photometric equipment
- ii. Filter funnels
- iii. Filter paper
- iv. pH meter
- v. Separatory funnels, 1000 ml, Squibb form, with ground glass stoppers and TFE stopcocks minimum of eight are required.

12. Phosphorus

The main source of phosphorus is due to the putrefaction of the hide substance. Vanadomolybdophosphoric Acid Calorimetric Method is used for the estimation of phosphorus.

Principle
In a dilute orghophosphate solution, ammonium molybdate reacts under aid conditions to form heteropoly acid (molybdophosphoric acid). In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to phosphate concentration.

13. Sampling techniques

The composition of an effluent sample is also dependent upon the sampling technique. There are two main methods that are acceptable.

1. Composite: samples taken over a 24 hour period and mixed together.
2. Spot samples: a single sample is taken for analysis if there is provision for collection and equalize the effluent discharged from 24 hours operation.

Ideally, composite samples should be taken by automatic sampler, with 24 samples taken at 1 hour intervals and mixed before analysis. If charges are made, then these are normally based on these values.

Where spot samples are taken, there are usually allowances for variation in effluent strength, often allowing a 50% increase in strength although this may not apply to all components.

The position of the sampling head is important. If it is too low, then there is the possibility of sludge being drawn into the sampler. This is also an important point when spot samples are taken as these are often manual. The sampling point should always be the same to reduce variables.

Duplicate samples

When samples are taken by an authority a duplicate sample should be held by the tannery. The sample should be shaken before the duplicate is poured, and the sample bottle should be clean, fully filled, airtight and kept under cold conditions. It is not unknown for samples to be incorrectly identified, or mistakes in analysis. Duplication always gives a visual check against the original and the chance for a second analysis if there are reasons for doubt.

14. Toxicity of effluent components

The toxicity of effluent components following dilution in surface waters is a complex subject and there is a shortage of specific data. This is due to the wide variety of aquatic life, the nature of individual components, and their degradation rate both in suspension and as part of a sediment. It is not possible to be specific for complex and multiple components of effluent and the effects on fish, invertebrates, algae and daphnia can be quite different.

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

Environmental Quality Standards are also used as a method of control for the protection of aquatic life, based on fate, behavior and aquatic toxicity. Much of this information is drawn from research data covering a variety of sources and species to find the most sensitive. Considerable data is often available to form conclusions, but when data is scarce conclusions may include expert judgment. The EQS may be defined as the concentration of a substance that must not be exceeded if a specific use of the aquatic environment is to be maintained.

Regarding metals that might be present in the tannery effluents – chromium, aluminum and perhaps zirconium, these are all classed as "high/moderate-acute" and "chronic toxicity" to organisms and may accumulate. An acute effect may be defined as having a specific effect up to 96 hours on fish, and chronic effects may need a 21 day test period or even involve full life cycles including counting of eggs and their fertility.

The toxicity of many metals also varies according to pH, temperature and water hardness. With reference to Cr 3+, investigation have been performed on fish (unspecified) under condition of exposure insufficient to cause severe toxicity, but sufficient to cause visual changes in behavior. These dosages were at the level of 0.2 mg/l. It is understood however, that daphnia has an even grater sensitivity, thus presenting a potential hazard to the fish food chain.

Zinc and copper described as high/acute and chronic toxicity to aquatic life have maximum levels of 0.3 mg/l total and 0.04 mg/l (dissolved) respectively as given in the Standards required by *E.C. Fish Directive* for salmon. Similar toxicity definitions apply to Cr 3+, and it is stated that dosages of 0.2 mg/l caused behavior change in fish (unspecified). In the absence of more specific data, loadings in these orders might be considered as 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 required for *EC Fish Directives* are presented in the table:

Suspended solids	< 25 mg/l
BOD/5 days	< 5 mg/l
Ammonia (as NH_3)	< 0.025 mg/l
Kjeldahl Nitrogen	< 0.78 mg/l

It should be noted that there are no values for sulphides, but the presence of sulphides will be included in the BOD analysis.

Annexure 2

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ARGENTINA – CHINA (page 1/10)

Country	**ARGENTINA**		**AUSTRALIA**		**AUSTRIA**		**BRAZIL**		**CHINA (Beijing)**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	5.5 - 10	5.5 - 10	6.0 - 9.0	6.0 - 10.0	6.5 - 8.5	6.0 - 9.5	5.0 - 9.0		6.0 - 9.0	6.0 - 9.0
2. Temperature °C	45	45	45	38	30	30	<40	40		35
3. Conductivity µS/cm										
4. Suspended solids mg/l			60	*	70	150			200	500
5. Settleable solids ml/l	0.5	0.5					1.0			10
6. BOD_5 mg O_2/l	50	200	40	*	25		60		150	500
7. COD mg/l	250	700			200				300	500
8. TDS mg/l										
9. Sulphide mg S^{2-}/l		1		1 - 5	0.1	2.0	0.2	5	1	10
10. Chrome (III) mg/l								5	1.5	2.0
11. Chrome (VI) mg/l					0.1	0.1				0.5
12. Chrome total mg/l	0.5	2	0.3	1 - 20	1.0	3.0	0.5		1.5	
13. Chlorides (as Cl) mg/l	*	*	*	*						
14. Sulphates (as SO_4) mg/l	*	1,000		2,000		*				
15. Ammonia mg N/l	3	10		100 - 200	15	*	5			
16. TKN mg N/l	10	30			*		10			
17. Phosphorus mg P/l					2.0		1			
18. Oil/grease mg/l	100	100		100 –1,000	20	100	20 - 30	100		100
19. Phenols mg/l	0.5	0.5	0.05 - 0.5	100			0.1 - 0.5			
20. Detergents mg/l										
21. Solvents mg/l										
21.1. Hydrocarbons mg/l			none	30	10	20				
21.2. Nitrogenous mg/l			none	none						
21.3. Chlorinated mg/l	1	2	none	5	0.5	0.5				

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

COLOMBIA – DENMARK (page 2/10)

Country	**COLOMBIA**		**COSTA RICA**		**CROATIA**		**CZECH REPUBLIC**		**DENMARK**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH		5 - 9	5 - 9	6 – 9	*	6.5 - 9.0			6.5 - 8.5	6.5 - 9.0
2. Temperature °C	40		15 - 40	<40	*	40			30	35
3. Conductivity µS/cm										
4. Suspended solids mg/l		1,000	200	500	*	400			30	
5. Settleable solids ml/l			1	1	*	15				
6. BOD$_5$ mg O$_2$/l			400	300	*	450	50			
7. COD mg/l		1,000	600	1,000	*	700	300			
8. TDS mg/l				1,500						
9. Sulphide mg S^{2-}/l			25		*	1	2		2	
10. Chrome (III) mg/l					*					
11. Chrome (VI) mg/l					*					
12. Chrome total mg/l	5		1.5	2.5	*		2		0.2	2
13. Chlorides mg/l				500	*					
14. Sulphates mg/l				500	*	300			300	
15. Ammonia mg N/l					*	15			2.0	
16. TKN mg N/l					*	80			5	
17. Phosphorus mg P/l										
18. Oil/grease mg/l		250	30	100	*	100			5	
19. Phenols mg/l			1	5	*	1.5				
20. Detergents mg/l										
21. Solvents mg/l					*	trace				
21.1. Hydrocarbons mg/l				20						
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l				0.5						

Notes: *specific requirements have to be fulfilled
Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

EGYPT – GREECE (page 3/10)

Country	**EGYPT**		**FINLAND**		**FRANCE**		**GERMANY**		**GREECE**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	6.0 - 9.0	6.0 – 10.0	6.0 - 10.0	6.0 - 10.0	5.5 - 8.5	6.5 - 8.5		6.5 - 10.0	6.5 - 9.0	6.5 - 9.0
2. Temperature °C	35	0	35	35	30	30		35	28 - 35	35
3. Conductivity µS/cm	--	--								
4. Suspended solids mg/l	30	500	*	*	35	600			25 – 50	500
5. Settleable solids ml/l	--	5-10							0 - 0.5	10
6. BOD_5 mg O_2/l	20-30	400	*	*	30	800	25		15 - 40	500
7. COD mg/l	30-40	700	*	*	125	2,000	250		45 - 150	1,000
8. TDS mg/l	800-1,200	2,000								
9. Sulphide mg S^{2-}/l	1	10	5	5		2	2	2	1 - 2	1
10. Chrome (III) mg/l			0 - 0.5	0 - 0.5	1.5	1.5			0.1 - 2	2
11. Chrome (VI) mg/l			none	none	0.1	0.1			0.02 - 0.5	0.5
12. Chrome total mg/l	0.05	5-10	10	20			1	1	2.5	2.5
13. Chlorides mg/l	--	--		2,500						
14. Sulphates mg/l	--	--		400				*	1,000	1,500
15. Ammonia mg N/l	100	100		50			10	*	10 - 20	25
16. TKN mg N/l	--	--			30	150				
17. Phosphorus mg P/l							2			
18. Oil/grease mg/l	100	100						*	5 - 20	40
19. Phenols mg/l	0.001-0.002	--		50	0.1	0.1		*	0.25 - 0.5	5
20. Detergents mg/l	0.05	0.005								
21. Solvents mg/l			3	3				*		
21.1. Hydrocarbons mg/l					10	10			0.2	
21.2. Nitrogenous mg/l									0.1 - 0.2	
21.3. Chlorinated mg/l					AOX 5	AOX 5	AOX 0.5		1	

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

HUNGARY – IRELAND (page 4/10)

Country	**HUNGARY**		**INDIA**		**INDONESIA**		**IRAN**		**IRELAND**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	5.0 - 10.0	6.5 - 10.0	5.5 - 9.0	5.5 - 9.0	6.0 - 9.0		6.5 - 8.5		7.5 - 10.0	7.5 – 10.0
2. Temperature °C			40 - 45	40 - 45						
3. Conductivity µS/l										
4. Suspended solids mg/l			100	600	150	150	40		800 – 1,000	800 – 1,000
5. Settleable solids ml/l										
6. BOD_5 mg O_2/l			30	500	150	150	30		500 – 1,700	500 – 1,700
7. COD mg/l	50 - 150		250		300	300	40		1,500–2,600	1,500–2,600
8. TDS mg/l			2,100	2,100						
9. Sulphide mg S^{2-}/l	0.01 - 5	1	2	2			2		5 - 35	5 - 35
10. Chrome (III) mg/l	2.0 - 5.0	5	2	2			3		15	15
11. Chrome (VI) mg/l	0.5 - 1	1	0.1	0.1			0.5		0.1	0.1
12. Chrome total mg/l		5	2	2	2	2				
13. Chlorides mg/l			1,000	1,000						
14. Sulphates mg/l		400	1,000	1,000			400			
15. Ammonia mg N/l	2 - 3	200	50	50	10	10	3.5		15 - 200	15 - 200
16. TKN mg N/l										
17. Phosphorus mg P/l							4			
18. Oil/grease mg/l	8 - 50	60	10	20	5	5			30	30
19. Phenols mg/l							1		0.05	0.05
20. Detergents mg/l							1.5			
21. Solvents mg/l										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l									0.05	0.05

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ITALY – NETHERLANDS (page 5/10)

Country	**ITALY**		**JAPAN**		**KENYA**		**MEXICO**		**NETHERLANDS**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	5.5 - 9.5	5.5 - 9.5	5.0 - 9.0	5.0 - 9.0	6 - 9	6.0 - 9.0	6 - 9		6.5 - 8.5	6.5 - 10.0
2. Temperature °C	30 - 35	30 - 35			25				30	30
3. Conductivity µS/cm										
4. Suspended solids mg/l	40 - 80	200	200	00-300	30	300	200		80	*
5. Settleable solids ml/l							5.0			
6. BOD$_5$ mg O$_2$/l	40	250	160	160	20	450	200		5	*
7. COD mg/l	160	500	160	160					*	*
8. TDS mg/l										
9. Sulphide mg S^{2-}/l	1	2	2	2			0.1		*	*
10. Chrome (III) mg/l		4								1
11. Chrome (VI) mg/l	0.2	0.2					0.1		none	none
12. Chrome total mg/l	2	4	2	2	1		1.0		0.05	2
13. Chlorides mg/l	1,200	1,200				3,000			200	*
14. Sulphates mg/l	1,000	1,000				100			150	300
15. Ammonia mg N/l	10 - 15	30				100			*	*
16. TKN mg N/l									3	
17. Phosphorus mg P/l			1							
18. Oil/grease mg/l	20	40	30	30 - 50	trace	100	30		*	*
19. Phenols mg/l	0.5	1	5	5	2					
20. Detergents mg/l										
21. Solvents mg/l									none	none
21.1. Hydrocarbons mg/l	0.2	0.4								
21.2. Nitrogenous mg/l	0.1	0.2								
21.3. Chlorinated mg/l	1	2								

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

NEW ZEALAND – POLAND (page 6/10)

Country	**NEW ZEALAND**		**NICARAGUA**		**PAKISTAN**		**PHILIPPINES** Marine Coastal water		**POLAND**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH		6.0 - 9.0	6 - 9	6 - 10	6 - 9	6 - 9	6.5 -9.0	6-9	6.5 - 9.0	
2. Temperature °C		55		50	40				35	
3. Conductivity µS/cm										
4. Suspended solids mg/l			150	400	200		90	200	35	
5. Settleable solids ml/l			5							
6. BOD_5 mg O_2/l			120	400	80		80	120	30	
7. COD mg/l			250	900	150		150	250	150	
8. TDS mg/l				1,500					2,000	
9. Sulphide mg S^{2-}/l		1 - 5	0.2	5	1				0.2	
10. Chrome (III) mg/l									0.5	
11. Chrome (VI) mg/l				0.5			0.2	0.5	0.2	
12. Chrome total mg/l		5 - 50	10	3.5	1					
13. Chlorides mg/l				1,500	1,000				1,000	
14. Sulphates mg/l				1,500	1,000				500	
15. Ammonia mg N/l					40				6	
16. TKN mg N/l									30	
17. Phosphorus mg P/l									5	
18. Oil/grease mg/l			30	150	10		10	15	50	
19. Phenols mg/l			0.1	1	0.3				0.5	
20. Detergents mg/l				10					10n.i+5i*	
21. Solvents mg/l										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l										

Notes: *specific requirements have to be fulfilled

**Present the values after year 2000

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

SOUTH AFRICA – TANZANIA (page 7/10)

Country	**SOUTH AFRICA**		**SPAIN**		**SRI LANKA**		**SWITZERLAND**		**TANZANIA**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	5.5 - 9.5	5.5 - 12.0	5.5 - 9.5	8 - 10	5.5 - 9.0		6.5 - 8.5	6.0 - 9.5	5.5 - 9.0	
2. Temperature °C	35	43	30				30	40		
3. Conductivity µS/cm										
4. Suspended solids mg/l	25	400 – 2,000	80 - 300	500 - 750	100		20		100	
5. Settleable solids ml/l	N/S	N/S	0.5 - 2							
6. BOD$_5$ mg O$_2$/l	N/S (10)	N/S (200-1400)	40 - 300	750 – 1,000	60		20		30	
7. COD mg/l	30	2000-5,000	160 - 500	1500 – 2,500	250					
8. TDS mg/l										
9. Sulphide mg S^{2-}/l	1	5-50	1 - 2	1 - 20	2.0		0.1	1		
10. Chrome (III) mg/l	0.5	N/S	2 - 4				2	2		
11. Chrome (VI) mg/l	0.05	N/S	0.2 - 0.5	0.5	0.5		0.1	0.5	0.1	
12. Chrome total mg/l	0.5	5 - 50		3 - 5	2.0		2	2		
13. Chlorides mg/l	N/S	1,000	2,000	2,000	1,000		200		1,000	
14. Sulphates mg/l	N/S	500 – 1,000	2,000	2,000				300		
15. Ammonia mg N/l	10	20 - 30	15 - 50	85						
16. TKN mg N/l	N/S	50								
17. Phosphorus mg P/l										
18. Oil/grease mg/l	2.5	50 - 100	20 - 40	150	10.0		20			
19. Phenols mg/l	0.1		0.5 - 1	2	1.0		5	5		
20. Detergents mg/l										
21. Solvents mg/l:	N/S	N/S								
21.1. Hydrocarbons mg/l	N/S	N/S	none	none			20	20		
21.2. Nitrogenous mg/l	N/S	N/S								
21.3. Chlorinated mg/l	N/S	N/S					0.1	0.1		

Notes: *specific requirements have to be fulfilled

** N/S: No Standard or Not specified

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

THAILAND - UNITED KINGDOM (page 8/10)

Country	**THAILAND**		**TUNISIA**		**TUTKEY**		**UGANDA**		**UK**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	5.5 - 9.0		6.5 - 8.5	6.5 - 9.0	6 - 9	6 - 10	6.0 - 8.0		6.0 - 9.0	6.0 - 10.0
2. Temperature °C	40		25	35		40	20 - 35		25	40
3. Conductivity µS/cm										
4. Suspended solids mg/l	150		30	400	150	350	50		30 - 50	500–1,000
5. Settleable solids ml/l			0.3							
6. BOD_5 mg O_2/l	20 - 60		30	400	100	250	30		20 - 30	
7. COD mg/l			90	1,000	200	800	100			2,000–6,000
8. TDS mg/l	5,000						1,000			
9. Sulphide mg S^{2-}/l	1		0.1	3	1	2	1.0		1	2 – 5
10. Chrome (III) mg/l	0.75		0.5	2					2 - 5	10 – 35
11. Chrome (VI) mg/l	0.25		0.05	0.5	0.3		0.05		0.1	0.1
12. Chrome total mg/l					2	5	1.0		1 - 2	1 – 20
13. Chlorides mg/l			600	700			30		4,000	5,000
14. Sulphates mg/l			400	600		1700	500			1,000–1,200
15. Ammonia mg N/l							10		100	10 – 100
16. TKN mg N/l			1	100		100	10			
17. Phosphorus mg P/l							10			
18. Oil/grease mg/l	15				20	100	10			50 - 500
19. Phenols mg/l	1					10	0.2			
20. Detergents mg/l							10			
21. Solvents mg/l									none	none
21.1. Hydrocarbons mg/l							*		none	none
21.2. Nitrogenous mg/l							*		none	none
21.3. Chlorinated mg/l							*		none	none

Notes: *specific requirements have to be fulfilled
Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

URUGUAY – ZAMBIA (page 9/10)

Country	**URUGUAY**		**USA**		**VENEZUELA**		**VIETNAM**		**ZAMBIA**	
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	6.0-9.0	5.5-9.5	6.0-9.0	6.0-10.0	6.0-9.0	6.0-9.0	5.5-9.0	5.0-9.0	6.0-9.0	
2. Temperature °C	30	35		35			40	45	40	
3. Conductivity µS/cm									4,300	
4. Suspended solids mg/l	150		60		60	400	100	200	100	
5. Settleable solids ml/l		10							0.5	
6. BOD$_5$ mg O$_2$/l	60	700	40		60	400	50	100	50	
7. COD mg/l					350	1,000	100	400	90	
8. TDS mg/l	5,000								3,000	
9. Sulphide mg S^{2-}/l	1	5		24	0.5	2	0.5	1.0	0.1	
10. Chrome (III) mg/l				8-19			1.0	2.0		
11. Chrome (VI) mg/l					0.5	0.5			0.1	
12. Chrome total mg/l	1	3	1	8-19	2	3	2.0	2.0		
13. Chlorides mg/l						300			800	
14. Sulphates mg/l						400			1,500	
15. Ammonia mg N/l	5								10	
16. TKN mg N/l					10	80	60	60	15	
17. Phosphorus mg P/l	5								1	
18. Oil/grease mg/l	50	200			20	150	10	30	20	
19. Phenols mg/l	0.5			10	0.5	0.5			0.2	
20. Detergents mg/l	4								2.0	
21. Solvents mg/l										
21.1. Hydrocarbons mg/l									10	
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l									0.5	

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ZINBABWE (page 10/10)

Country	**ZIMBAWBE**									
Parameter	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer
1. pH	6.8-9.0	> 7.5								
2. Temperature °C	45 max	45								
3. Conductivity µS/cm										
4. Suspended solids mg/l	600	6,000								
5. Settleable solids ml/l	10									
6. BOD$_5$ mg O$_2$/l	1,000									
7. COD mg/l	3000	6,000								
8. TDS mg/l										
9. Sulphide mg S^{2-}/l		200								
10. Chrome (III) mg/l										
11. Chrome (VI) mg/l										
12. Chrome total mg/l	10	10								
13. Chlorides mg/l	1,000	4,000								
14. Sulphates mg/l	1,000	300								
15. Ammonia mg N/l										
16. TKN mg N/l										
17. Phosphorus mg P/l	30									
18. Oil/grease mg/l	50	450								
19. Phenols mg/l										
20. Detergents mg/l	20									
21. Solvents mg/l										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l										

Notes: *specific requirements have to be fulfilled

Figures in the table were compiled from various sources and cannot be considered as official.

Annexture 3

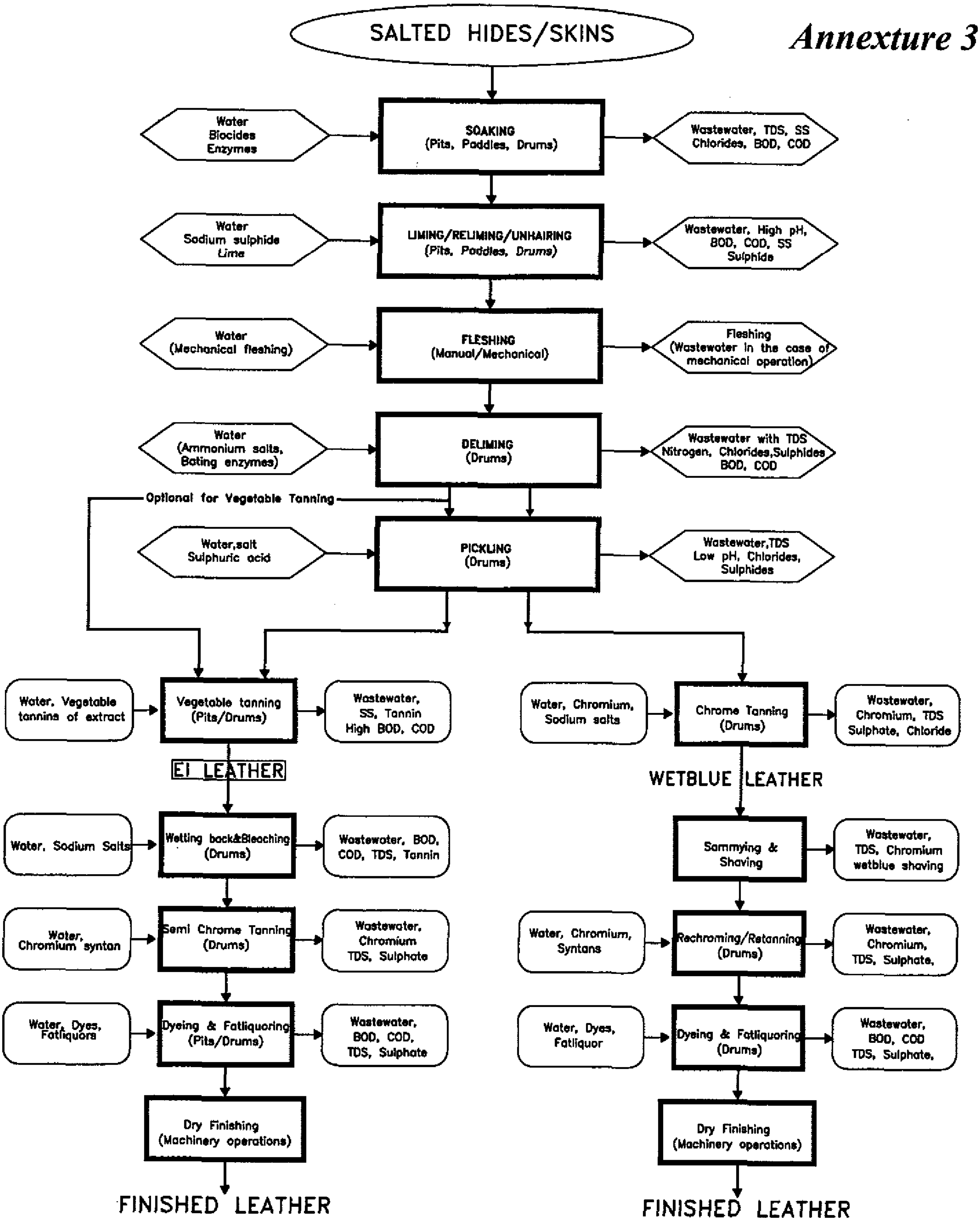
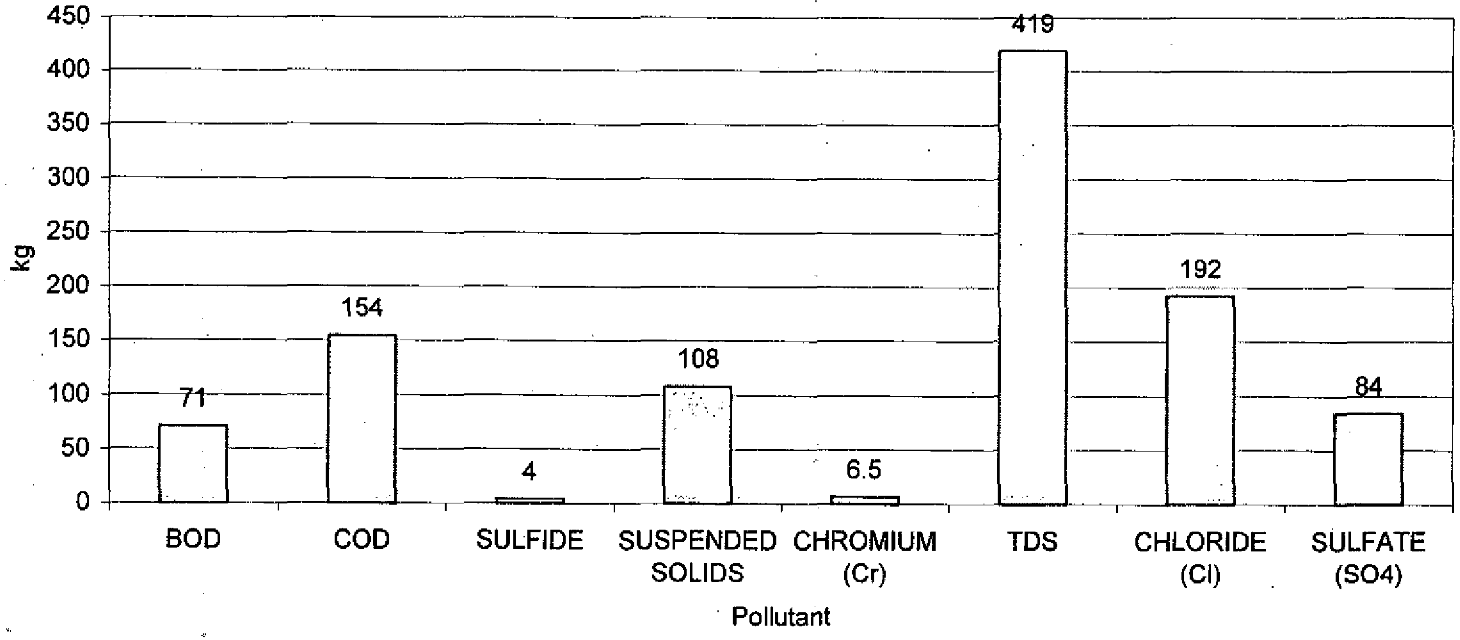


Figure 3.1. Flowchart of leather processing

Figure 3.2. POLLUTIONAL DISCHARGE PER TON OF HIDES /SKINS PROCESSED FROM RAW TO FINISH



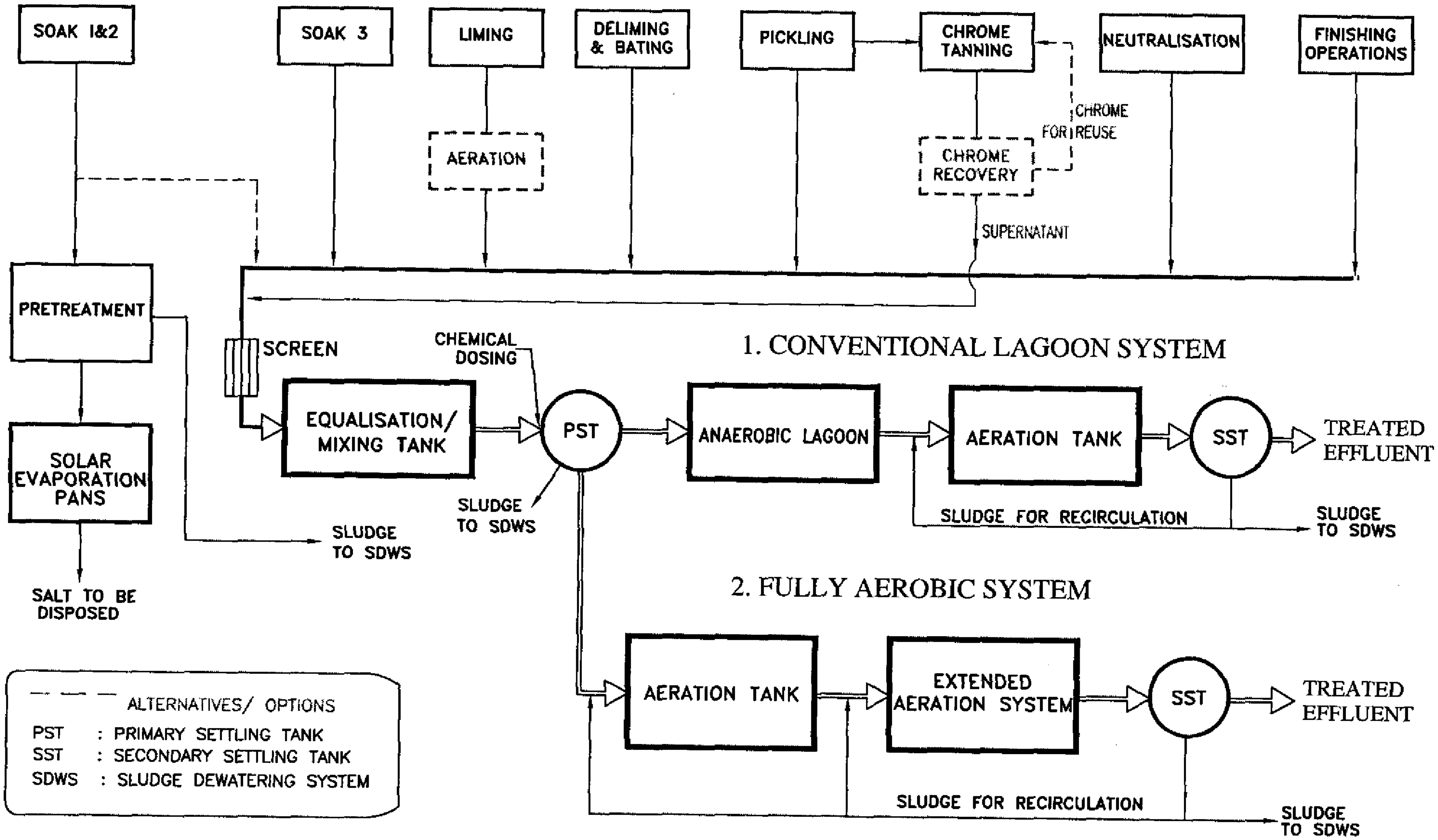


Figure 3.3. Tannery effluent treatment systems