International
Journal
Of Advanced Research in Engineering& Management (IJAREM)
ISSN: 2456-2033 || PP. 110-117

Polution and Control Measures in Leather Tanning and Finishing Processes: A Review

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Abstract Tanning is the process by which animal hides and skins are converted into leather. Basically, leather is formed by the reaction of collagen fibers with tannin, chromium, alum or other tanning agents which pollute the environment. Tanneries generate wastewater in the range of 30-35 L /kg skin/hide processed with variable p Hand high concentrations of suspended solids, BOD, COD, tannins and chromium (Nandy*et al.*,1999).In developing and newly industrialized countries solid waste and wastewater treatments facilities are notstate of the art due to cost and technical know-how and there is a high labour content in leather processes. Therefore, adequate knowledge of pollution prevention and control measures should be thought and practised.
Keywords: Tannery effluents; prevention; environment.

Tanning Industry: A Global Outlook

Leather is a globally acclaimed product and there is an ever increasing demand forleather and its related products. The current trade value of the leather industry isestimated to be approximately US$ 70 billion per year. The industry in total producesabout 18 billion square feet of leather a year, with developing countries producing over60% of the world's leather. About 65% of the world production of leather is estimated to go into leather footwear. Its major expansion has taken place in developing and newlyindustrialized countries rather than in developed economies. The United States, Germany, and other European countries remainmajor importers of leather products. Countries such as China, India, Thailand, andIndonesia dominate the export of leather and leather products (Danish Technological Institute, 1992).

Tanning Process

The four leather tanning processes; beam house; tanning; retan, color and fatliquor; and finishing and the waste generated have already been reported in literature (Sreeram and Ramasamy, 2003; Stoop, 2003) and an overview is presented in Figure1.

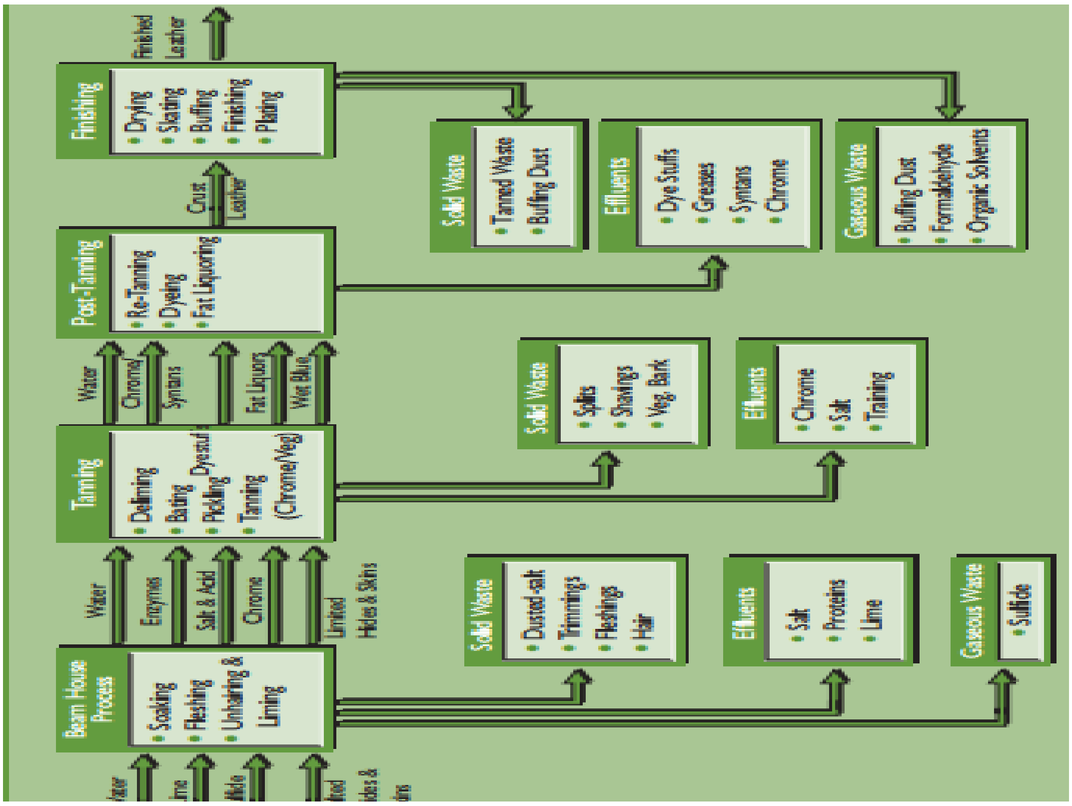

Figure1: Process Sequences and Nature of Effluents in Tanneries (Sreeram and Ramasamy, 2003;)

Sources and types of pollutants generated in leather processing

Wastewater: During leather processing, the hides and skin undergoes a series of pre-tanning, tanningand post-tanning operations. Water is an input material used in large quantities most inall the processes of tanning and finishing. The washing of process equipment and floor are inevitable operations in every tannery. Thequantity of water used in processing a kg of hide/skin is about 30–35 litres and varies between tanneries and process (DTI, 1992) As shown in table 1 every tanning chemical in found in tannery wastewater as pollutants.

Chemicals	Added in process	In/on leather & splits	Wasted
Chrome oxide, Cr_2O_3	25	12	13
Organic tannins	25	20	5
Fat liquors	22	17	5
Dyestuffs	5	4	1
Acids, bases, salts	191	-	191
Tensides	3	-	3
Enzymes	5	-	5
Finishing products	100	12	88
Total	452	72	380

Table 1. Mass balance in leather processing kg/tone of wet- salted hide (UNIDO,2011;US EPA 2002)

Wastewater from the beamhouse processes (e.g. soaking,fleshing, de-hairing, and liming) and from associated rinsing is generally collected together. The wastewater may contain hide substance, dirt,blood, or dung and therefore have significant loads of organicmatter and suspended solids.While wastewater from tanyard processes, deliming and bating maycontain sulfides, ammonium salts, and calcium salts and isweakly alkaline. After pickling and tanning processes, the mainwastewater contaminants depend on the tanning techniquesused. Finishing wastewaters may contain lacquer polymers,solvents, color pigments and coagulants (Buljan, 2004)
The potential environmental and health impacts of tanning wastewaterare significant. A composite untreatedwastewater, 20 to 80 cubic meters per metric ton(m3/t) of hide or skin, is turbid, colored, andfoul smelling. It consists of acidic and alkalineliquors, with chromium levels from 100 to 400milligrams per liter (mg/L), sulfide levels from200 to 800 mg/L, nitrogen levels from 200 to1,000 mg/L, biochemical oxygen demand(BOD5) levels from 900 to 6,000 mg/L, (usuallyranging from 160 to 24,000), chemical oxygendemand (COD) (ranging from 800 to 43,000mg/L in separate streams with combined wastewater levels of 2,400 to 14,000 (mg/L), chloride (200 to 70,000 mg/L in individualstreams and 5,600 to 27,000 mg/L in thecombined stream) and high levels of fat. Suspended solids are usually half of chloridelevels. It may also contain residues of pesticidesused to preserve hides during transport andpathogens at significant levels. Significantvolumes of solid wastes are produced, including trimmings, degraded hide, and hairfrom the beamhouse processes. The solidwastes can represent up to 70% of the (wet) weight of the original hides. In addition, largequantities of sludge's are generated. Decayingorganic material produces strong odors.Hydrogen sulfide is released during de-hairing. Ammonia is released during de-liming. Airquality may be further degraded by release of solvent vapors from spray application,degreasing, and finishing for example, dye application(UNEP-UNIDO, 1991;OECD,2014))

Reduction of water input: General wastewater managementmeasures and process optimization in tanning facilities shouldaim at reducing the need and intensity of end-of-pipe treatmentthrough implementation of wastewater prevention measures,including:Reduction of water consumption, through recycling ofprocess streams; Use of 'batch" instead of 'running water' washes;Segregation of wastewater streams (e.g. soaking liquors,sulfide-rich lime liquors, and chrome-containing liquors) toimprove treatment speed and efficiency.. Segregation ofwater streams also helps to isolate particularlyconcentrated or toxic compounds, such that they can beremoved separately and possibly recovered for reuse;Use of short (e.g. low-water content) floats in the tanningcycle (e.g. floats using from 20 to 40 percent water withrespect to normal floats), which allow for water savings ofup to 70 percent and facilitate chrome fixation(whencombined with increased temperature at the end of thetanning operation); Chemical substitution for less toxic and morebiodegradable chemicals, as specified below; Split hides before de-liming and tanning, when feasible, toallow improved penetration of the tanning chemicals intofiber structure thereby reducing chemical usage(UNEP-UNIDO, 1991).

COD/BOD and Suspended Solids: Approximately 75 percent of the organic load (measured as biochemical oxygen demand [BOD] and chemical oxygen demand[COD]) is produced in the beamhouse, with the maincontribution coming from liming / de-hairing processes. De-hairingis also the main generator of total suspended solids. Anadditional source of COD / BOD is the degreasing process.Total COD/BOD concentrations can reach 200,000 mg/l.(Danish Technological Institute.1992).

Preventive measures: Measures to reduce the organic load of these wastewaterstreams include the following:Screen wastewater to remove large solids;Use an enzymatic de-hairing process and recover hair forresale, reducing COD by up to 40–50 percent);If conventional lime de-hairing process is used, filterwastewater to recover hair before dissolution. This mayreduce COD by 15–20 percent and total nitrogen by 25–30percent in mixed tannery effluent;Recycle liming float which may reduce COD by 30–40percent; nitrogen by up to 35 percent, sulfide use by up to40 percent, and lime use by up to 50 percent; Use easily degraded ethoxylated fatty alcohols, instead of ethoxylated alkylphenols, as surfactants in degreasing;Use carbon dioxide (CO2) de-liming (e.g. for light bovinehides of less than 3 mm thickness). For thicker hides, theprocess requires an increase in the float temperature (up to 35°C), and / or process duration, and / or the addition ofsmall amounts of de-liming auxiliaries (UNEP-UNIDO, 1991;Danish Technological Institute,1992)

Salts and Total Dissolved Solids: Salting and other tannery processes contribute to the presenceof salts / electrolytes in wastewater streams, measured as TotalDissolved Solids (TDS). Approximately 60 percent of totalchloride is produced from sodium chloride used for curing and in preservation which issubsequently released in the soaking effluent.The rest isgenerated mainly from pickling and, to a lesser extent, tanning and dyeing processes (Environment Australia,1999)..

Being highly soluble and stable, itis not affected by effluent treatment and nature, thus remaining as a burden on the environment. Considerable quantities of salt are produced by industry and levels can rapidly rise to the maximum levelacceptable for drinking water. Increased salt content in groundwater, especially in areas of high industrialdensity, is now becoming a serious environmental hazard. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases throughevaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system andmay ultimately end up in the groundwater.

Additional contributors to TDS includethe use of ammonium chloride and sodium sulfate. The TDSconcentrations may reach 15,000 mg/l in tannery effluents.Disposal of waste-neutral electrolyte is a significant challengefor leather manufacturing, particularly for those facilities locatedin land-locked areas(Danish Technological Institute. 1992).

Preventive measures: Measures to reduce TDS loads from rawmaterial preservation and processing include the following:· Use of natural drying of small skins at facilities in suitablewarm, dry climates;Use of chilling for short-term preservation of freshlyprocessed hides or skins, and / or use of antiseptics toincrease storage time;Undertake trimming and, where possible, pre-fleshingbefore curing or other pre-tanning operations;Use of mechanical or manual removal of salt from hidesand skins before soaking;Installation of salt-free pickling systems, and use of non-swelling polymeric sulphonic acids (this may affect leathercharacteristics); Use of ammonium-free de-liming agents (e.g. weak acids oresters) or CO_2 de-liming instead of ammonium salts;Using short floats in tanning to reduce chemical loads; Chrome fixation during tanning is enhanced by the use ofhigh-exhaustion tanning process techniques including short floats; increased temperature; increased tanning times;increased basification; and decreases in the level ofneutral salts3;Direct recycling of the pickling float, where practical (iftanning is performed in the float, only partial recycling ofthe exhausted tanning bath is possible);Direct recycling of tanning floats Recycling of supernatant from chrome recovery to enhancechrome savings;Use of liquid dyes and syntans(Buljan,1997; Buljan, 2007)

Sulfides: Inorganic sulfides (NaHS or Na_2S) and lime treatment are used in the de-hairing process, which may result in sulfide-containingliquors in the wastewater effluent. Sulphides pose many problems. Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterized by a smell of rotten eggs, a severe odour problem occurs. In its toxicity, hydrogen sulphide is comparable to hydrogen cyanide; even a low level of exposure to thegas induces headaches and nausea, as well as possible eye damage. At higher levels, death can rapidly setin, and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded (UNIDO, 2011; Environment Australia,1999).).

Preventive measures: Although a total substitution ofsulfides used in this process is not practical, especially forbovine hides, the following approaches are recommended toreduce sulfide use and discharge. Use an enzymatic de-hairing process; For conventional lime de-hairing processes, use sulfide andlime in a 20–50 percent overall solution;Maintain sulfide-containing wastewater at an alkaline pH(>10) level. The conventional treatment is lime and sulfidewastewater oxidation (catalytic oxidation tanks, or aerationtanks). Care should be taken to avoid an accidental pHvalue dependent (pH<7) release of hydrogen sulfide (H_2S),arising from, for example, inappropriate mixing of alkaline and acid streams, and uncontrolled release from denitrification steps (Buljan, 2007;Environment Australia.1999).).

Nitrogen Compounds in wastewater: Significant nitrogen loads and resulting discharge of ammonianitrogen are typically associated with tanning processes. Theuse of ammonium salts in the process is a main source ofammonia nitrogen in tannery effluents (up to 40 percent). Othersources of ammonia nitrogen are dyeing and animal proteinsgenerated from beamhouse operations. The majority of totalnitrogen matter (measured as Total Kjeldahl Nitrogen, TKN) is discharged from the liming process in the beamhouseoperations, which, as a whole, account for approximately 85percent of TKN load from a tanning facility(World Bank and International finance cooperation, 1996)

Preventive measures: Prevention and control measures that reduce the organic load(COD / BOD5) may also reduce nitrogen levels. Additionalmeasures to reduce the nitrogen load in effluents include:· Use ammonium-free de-liming agents (e.g. weak acids oresters) if CO2 de-liming is not implemented;Where ammonia discharge might adversely affect the receiving water, include denitrification in waste water treatment to convert ammonia nitrogen to nitrates, althoughcareful control and management is needed to limit thepotential risk of H_2S formation (OECD,2014).

Chromium and Other Tanning Agents: Trivalent chromium salts such as $Cr_2O_3$are among the most commonlyused tanning agents, accounting for the majority (approximately75 percent) of the chromium in the wastewater stream. Theremainder is typically generated from post-tanning wetprocesses, from stock drainage, and wringing. The reducingcharacteristics of tannery sludge serve to stabilize Cr(III) with respect to hexavalent chromium (Cr VI) content, as a result of the presence of organic matter and sulfide (UNIDO, 2000)

Preventive measures: The following measures should be taken to limit use anddischarge of chromium: Consider using alternative tanning agents in place of, or inaddition to, chromium, considering the toxicity andpersistence of the alternative agents as well as the use anddesired characteristics of the leather product.Avoid the use of chromium (VI), by limiting the type ofchromium employed to chromium (III); Recycle chrome tanning floats. This may reduce chromiumuse up to 20 percent in a conventional tannery process, and up to 50 percent in wool-on sheepskins. Liquorcontaining excess chromium may be precipitated, acidified, and then recycled. Reduce chromium concentration in the waste float by usinghigh-exhaustion chromium salts and alkaline products and /or increasing the float temperature; Avoid the use of Chromium because it can adsorb onto thesurface of organic particles of varying sizes and may notprecipitate out of solution. Care must be taken that these particles are not mixed with the tannery effluent anddischarged, using polyelectrolytes;Avoid disposal of chrome tanning sludge throughincineration, asalkaline conditions and presence of excessoxygen can lead to the conversion of Cr(III) into more toxicCr(VI) (World Bank and International finance cooperation 1996).

Offensive odour: Odours associated with tannery wastewater are difficult to quantify because they are caused by a wide variety ofcompounds and they are a nuisance that is more qualitative than quantitative – sensitive persons easilydetect very low concentrations of odoriferous substances in the air (Buljan, *et al* (1997) Bad air emissions from tanning facilities may be from the following sources:

Organic solvents: Organic solvents are used in degreasing and finishingprocesses. Untreated organic solvent emissions from thefinishing process may vary between 800 and 3,500 mg/m³ inconventional processes. Approximately 50 percent of VOCemissions arise from spray-finishing machines, and theremaining 50 percent from dryers. Chlorinated organiccompounds may be used and emissions released from soaking(Buljan,, 2004: UNIDO, 2000))

Preventive measures: Consider water-based formulations (containing lowquantities of solvent) for spray dyeing;Implement organic solvent-saving finishing techniquessuch as roller coating or curtain coating machines where applicable (e.g, application of heavy finish layers), andotherwise use spraying units with economizers and highvolume / low-pressure spray guns;Prohibit the use of internationally banned solvents;Control VOC emissions through the application ofsecondary control.Examples of industry-specific controlsinclude wet scrubbers (including the use of an oxidizingagent to oxidize formaldehyde), activated carbonadsorption, biofilters (to remove odors), cryogenictreatment, and catalytic or thermal oxidation(Buljan,2004; UNIDO, 2000)

Sulfides: Sulfides are used in the de-hairing process. Hydrogen sulfide(H_2S) may be released when sulfide-containing liquors areacidified and during normal operational activities (e.g.opening ofdrums during the de-liming process, cleaning operations / sludgeremoval in gullies and pits, and bulk deliveries of acid or chromeliquors pumped into containers with solutions of sodium sulfide).The main source of bad smell remains the stripping of hydrogen sulphide; it is not the concentration of sulphide per se, but the lowering of pH: the undissociatedH_2S is present only at pH below 10. H_2S is an irritant and asphyxiant. (UNIDO,2000)

Preventive measures: for sulfide emissions include: Prevention and control measuresfor sulfide emissions includethe following: Maintain a basic pH over 10 in facility equalizing tanks andsulfide oxidation tanks, alkalis like NaOH or lime may be added to achieve Ph> 9.5-10.;Prevent anaerobic conditions in sulfate-containing liquorsand sludge; Add manganese sulfate to treated effluent, as needed, tofacilitate the oxidation of sulfides;Where H_2S formation may occur, use adequate ventilationto capture the emissions, followed by treatment with wetscrubbers or biofilters (particularly for wastewater treatmentunits) (IUE,2004;Buljan,2005)

Ammonia: Ammonia emissions may be generated from some of the wetprocessing steps (e.g. deliming and dehairing, or during drying ifit is used to aid dye penetration in the coloring process).Prevention and control of ammonia emissions may be achievedthrough use of adequate ventilation , followed by wet scrubbingwith an acidic solution(UNIDO, 2000).

Raw hides and skins, putrefaction: Odors may result from raw hides and skins, putrefaction.Control odor problems by good housekeeping, such as minimal storage of flesh; Promptly cure raw hides; Reduce the time that sludge remains in the thickener, dewater thickened sludge by centrifugation or filter press, and dry the resulting filter cake. Sludge containing less than 30 percent solids may generate especially strong odors; Ventilate tannery areas and control exhaust from odorous areas (e.g. where wastewater sludge is thickened and dewatered), through use of a biofilter and / or a wet scrubber with acid, alkali, or oxidant (UNIDO,2011) .

Solid Waste: Solid waste includes salt from raw skin / hide dusting; raw skin /hide trimmings; hair from the liming / de-hairing process, which may contain lime and sulfides; and fleshing from raw skins /hides. Other solid waste includes wet-blue shavings, whichcontains chromium oxide (Cr_2 O_3); wet-blue trimming, which isgenerated from finishing processes and contains chromiumoxide, syntans, and dye; and buffing dust, which also contains chromium oxide, syntans, and dye. The reducing characteristicsof tannery sludge stabilize Cr(III) with respect to Cr(VI), due tothe presence of organic matter and sulfides(UNIDO,2011) .

Prevention and control measures: Prevention and control measures for solid waste include the following:Reduce inputs of process agents (particularly precipitation agents in wastewater treatment) to the extent practical; Segregate different waste / residue fractions to facilitate recovery and re-use (e.g. to manufacture pet toys, pet food, leather fiberboard);Recycle sludge as compost / soil conditioner or in anaerobic digestions for energy generation. Process sludge may be used for composting / agriculture after appropriate assessment for contaminants and potential impacts to soil and groundwater;Dispose of non-recoverable and non-recyclable waste and sludge by appropriate methods, depending on the waste hazard classification (COTANCE,2002).

Effluent and Emission Guidelines: Table 1 presents guideline values for process emissions and effluents. It is an indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. These guidelines are achievable under normaloperating conditions in appropriately designed and operatedfacilities through the application of pollution prevention andcontrol techniques discussed in this rewiew.

Pollutants	Units	Guideline Values
pH	S.U.	6-9
BOD_5	mg/L	50
COD	mg/L	250
Total Suspended solids	mg/L	50
Sulfide	mg/L	1.0
Chromium (hexavalent)	mg/L	0.1
Chromium (total)	mg/L	0.5
Chloride	mg/L	1000
Sulfate	mg/L	300
Ammonia	mg/L	10
Oil and Grease	mg/L	10
Total nitrogen	mg/L	10
Total Phosphorous	mg/L	2
Phenols	mg/L	0.5
Total coliform bacteria	MPN[a] / 100 ml	400
Temperature increase	°C	<3[b]

Table 2 waste water tanning pollutants limit (World Bank and International finance corperation,2007:US EPA.2002).

Conclusion

The treatment of tannery effluents is by now a well established cost intensive technology and two issues still pose serious challenges: High TDS (salinity) content is unaffected by treatment. This problem is especially pronounced in developing countries where mixing tannery effluent with domestic sewage or its discharge into the sea is not feasible, and the raw hides and skins are still preserved by salting. Relocation of tanneriesto the seaside is often not feasible, and desalination of treated effluent by reverse osmosis is veryexpensive. Also, effective utilization or safe disposal of sludge is a serious issue for local tanners.The only cost-effective solutions to both of these problems are pollution prevention and control detailed in this review.

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