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An Overview of Environmental Pollution Management in Tanning Unit

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Abstract

Leather industry is one of the oldest industries and also highly polluting industry in India. Tanning industry in India stands among the five top exports oriented industries. The unplanned growth of the leather industry, inadequate knowledge and inexperience in environment pollution management has caused several pollution problems which are yet to be solved at the desired level. In the present study a sincere attempt is made to cover all the important aspects relating to environmental pollution problems associated with this industry. In the present study, results have demonstrated that mostly all the stages of leather processing, individually and collectively have an impact on the environment. The quantity of chemicals used for processing, details of wastewater discharge processing capacity, and characteristics of wastewater released in various pre-tanning processes, characteristics of effluent from tannery have been studied. The treatment of liquid wastes generated by the Tanning unit has also been highlighted.

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Pollution

Introduction

Tamil Nadu is one of the largest producers of finished leather in the country. There are more than 1000 tanneries classified under Small Scale industries processing about 2 tons of hides and skins per day. There are eight major tanning clusters, located in Tamil Nadu viz., Ranipet, Ambur, Pernampet, Vaniyambadi, Erode, Dindugul, Trichy and Pallavaram. Tannery effluents are the most pernicious, offensive and deleterious of all industrial wastes that have posed a potent threat to environmental pollution. (Ros and Ganter1998) They contaminate air, surface and sub-soil waters and undermine the fertility of the soil. As a result of rapid strides taken by the leather industry, the menace of environmental pollution has assumed colossal proportions. The disposal of tannery wastes is the responsibility of the tanning industry. (Kadam, 1987) But the cost involved in their disposal according to specifications and regulation is beyond the resources of the industry. Due to industrial expansion, large quantities of industrial wastes are accumulating in environment and cannot be disposed without prior special treatments. Due to industrial enlargement, massive quantities of industrial wastes are accumulating in environment and can't be disposed while not previous special treatments (Belay, 2010). In particular, waste products from the mining and metal refining industries, sewage sledges and residues from power station and waste incineration plants can contain heavy metals at high concentrations.

Usually, these heavy metals can be leachated from the soil to the surface water system (Chang *et al.*, 1984; Dowdy *et al.*, 1991) at concentrations higher than they are allowed (CEC, 1986). Effluent disposal into the environment creates adverse effects by altering the normal physiochemical properties of soil and water (Kannan *et al.*, 2012).

Tannery effluents are of large scale environmental concern because they color and diminish the quality of water bodies into which they are released. Among heavy metals presents in sludge, Chromium is one of the most common. This metal exists in two stable oxidation states, trivalent and hexavalent Chromium. The trivalent Chromium state is less toxic and mobile, while hexavalent Chromium is easily soluble and 100 fold more toxic than trivalent Chromium. So, the reduction of Chromium (VI) to Chromium (III) is an attractive and useful process for remediation of Chromium (VI) pollution, and the technologies focusing on transformation of Chromium(VI) to Chromium(III) have accordingly received much more concerns (Vijayanand *et al.*, 2012). Tannery wastewaters are stratified because the highest pollutants among all industrial wastes. They are particularly giant contributors of Chromium pollution.

Materials and Methods

The water samples have been collected from the outlet of the tannery unit. In this present study, various physical and chemical parameters of water samples were determined using APHA (1998) Standard methods for the examination of water and waste water. The samples collected were analyzed for important physical and chemical parameters such as pH, alkalinity, acidity, BOD, COD, Chlorides, Total solids, suspended solids, and sulphate were determined using standard procedures. Also the above parameters were measured in waste water of the tanning process, such as- Soaking, Liming, deliming, Pickling, Chrome tanning, Neutralisation and dyeing processes. All the chemical constituents are expressed in mg/L (milligrams/liter).

Results and Discussion

Sodium chloride, Lime, Sodium sulphide, Ammonium chloride/Ammonium sulphate, Bate powder/ sulphuric acid, Basic chromium sulphate, vegetable tan extract, sodium sulphate, sodium carbonate, Sodium formate, pretanning syntax, syntax for retaining, fat liquor, dyes.

Solvents like trichloroacetic acid, kerosene, the quantum of chemicals used for processing 10,000 kgs of skins per day are shown in Table 1

Beam house operations include, Soaking, Liming and Deliming process. The principal raw materials used in tannery are hides and skins and they are received in wet salted or dry salted conditions. Soaking process consists of immersing the wet salted or dry salted hides and skins in water in pits for 6 to 24 hrs. In some tanneries wetting agents are also used during soaking. Nowadays some of the tanneries use either paddles or drums for the soaking process to reduce the duration of soaking and to economize the water consumption.

With regard to Water discharge it should be understood that the Tanning industry is one of the major industries consuming large quantity of water for processing of raw materials into leather. Tanneries draw water from their own wells and from river banks through tankers. Water used in the process are not measured. Since unskilled labourers are employed for beam house operations (for which pits are used), water consumption is more than for tanning and post-tanning (for which drums are used). Operations which include consumption of water for different sectional operations are given in Table 2.

Beamhouse operations consume 55% of total water while tanning and post tanning operations consume 45% of total water. As indicated in Table 3 the water used in different types of processinvolve batch operations and therefore waste water discharge from tanning industry is not a continuous flow, instead it is only an intermittent discharge. Figure 1 shows the Discharge pattern in Tanning industry. Water usage for leather process varies from tannery to tannery, region to region and also from season to season.

Characteristics of Effluents, include Soak Liquor Characteristics-Soak effluent is characterized by pH 7.35 to 7. It has high suspended solids in the effluent.It comprises of suspended impurities like dirt, dung and soluble material like blood adhering to the hides and skins during soaking; the salinity of the soak liquor is very high. The pH of the soak liquor is favourable for the growth of bacteria and hence the liquor undergoes putrefactionvery rapidly. Characteristics of soak liquor is given in Table 4.

In Liming effluent -Lime liquor contain suspended and dissolved lime and sodium sulphide. It is highly alkaline and is one of the heaviest of the fractions in terms of biochemical oxygen demand and suspended solids. This waste may contain high concentration of sulphides when sodium sulphide is used in the liming process. Also, the Unhairing and fleshing effluent is equally polluting, since this effluent from the unhairing operation contains mostly hair and sulphides. Fleshing operations discharges effluent with fatty and fleshy matter in suspension. The Deliming effluent -Spent deliming liquors that are discharged carry a significant pollution load in terms of BOD. In terms of Spent bate liquor, it should be noted thatthis waste contains a high amount of organic matter and ammoniacal nitrogen due to the presence of soluble skin proteins and ammonium salts used in bating. BOD is usually low. The Spent Pickle Liquor also carries a high amount of chloride and the waste is acidic.

To highlight Vegetable tanning effluent- the spent vegetable tan liquor is the strongest sectional waste in a composite tannery effluent.It has persistence of colour which is difficult to remove by chemical or biological method and a characteristic offensive odour. This is acidic in nature.

When it comes to Chrome tanning effluent it is imperative that the spent chrome tan liquor is greenish in colour and is highly acidic and this effluent contains a high amount of trivalent chromium.

However, the Dyeing and fat liquoring effluentis smaller in volume. The major constituents are dye and oil emulsions. Finally, the Composite effluentfrom a tannery is highly coloured and foul smelling. This includes lime, sulphide, soluble protein, fats, grease, chlorides, tannins, chromium sulphate, hair, flesh particles, bacterial inhibitors, wetting agent, oils, salts and dyes.

When it comes toPollutional load of the tanning unit, as is shown in Table 5. It is indicative that tanning unit discharges inorganic, non-degradable salts, in the form of $Cl^{-,}$ SO^{2-}_4, Cr^{3+}, $S^{2-.}$

These pollutants are thrown out as dissolved solids causing ground water pollution. It has been observed that the treated tannery effluents bear a straw yellow to light orange which are not aesthetically accepted despite the organic pollution being eliminated to the required level.

Treatability of waste water

Biodegradability of waste constituents are assessed by the ratio of BOD/ COD. This is considered to be biodegradable index of wastewater. This ratio determines treatability of waste water either by chemical or biological means. In Table 5, the BOD/COD ratio of different sectional wastes is shown. The BOD/COD ratio of wastes from finishing operations is less than that of Beamhouse wastes. Even though BOD/COD ratio of beamwaste is above 0.5, but due to presence of high amount of ammonium chloride, biological activity is inhibited. Chlorinated phenols are important compounds to be investigated due to the various mixtures used in the tanning industry and their ecotoxicity potential (UNEP 1994).

Vegetable tannins are also used to retan leather to impart certain specific desired. Pollutional load contribution by different sectional wastes to Beamhouse waste thereby leading to composite waste is shown in Table 5. It would be highly illuminating to project that pollutional load by Beamhouse wastes are more than Tanning and Post Tanning operational water. Among beamhouse wastes, liming alone contributes 47% of Cl^- Total composite. Presence of sulphides in the effluent retard rate of degradation of organics by aerobic organisms. The major contribution of sulphide to composite effluent is only through lime yard effluent.

Hence it is worth mentioning to segregate the sectional waste from the other-main-streams to be evaporated in solar evaporation ponds and scraped salts are disposed in sea. Alternatively the entire composite waste water after Physical, Chemical and Biological treatment may be treated. Physical and chemical processes are frequently employed to treat contaminated sites, but often do not destroy contaminants (Bouwer *et al.*, 1994).

Further Reverse Osmosis was used to remove the chloride such that to reach the effluent discharging standard. This modification of procedure may be technically viable, but the cost involvement is very high and also this technique demands a very trace level of organics in the wastewater which becomes highly impracticable due to certain environmental constraints.

Salinity or ionic strength can cause a small decrease in the solubility of non-polar organic compounds (e.g. naphthalene, benzene, toluene etc.) through a process known as the *salting-out effect* (Pepper *et al.*, 1996). In a study in Egypt, $NaCl_2$ concentration varied between 40,000 and 50,000 mg L in the effluent discharge in a tannery under study (Hafez *et al.*, 2002).

Treatment of tannery waste water

The following unit operations are employed for the treatment.

Equalisation cum settling tank/primary clarifier.
Anaerobic lagoon
Aerated Lagoon
Secondary settling tank/secondary clarifier.

Table.1 Quantity of chemicals used for processing 10,000kgs of skin/hide

Chemicals	Raw to finish	Process Raw to E.I	E.I to Finish
Na Cl	80		
Lime	600	600	
Na_2S	30	25	
Soda ash	2.5		
Na_2SO_3			20
NaOH	2.5	2.5	
$(NH_4)_2 SO_4$	10	10	
Wetting agent	2.5		
H_2SO_4	10		
Basic Chromium Sulphate	80		
Sodium formate	20		
Sodium Bicarbonate	10		
Syntan	20		
G.S. Powder	180		
Formic acid	10		
Fat liquor	55	70	

Table.2 Details of Wastewater Discharge Processing Capacity: 10,000 skins /day weight of each goat skin: 0.8 to 1.2 kg

S.No	Operation	Wastewaterdischarge (inm$^{3)}$ per day
	Beamhouse operations	
1	Soaking	80-90
2	Liming	55-60
3	Fleshing	32-38
4	Washing before delining	20-24
5	Delining and bating	9-10
6	Scudding operation	2-3
7	Degreasing	30-35
	Tanyard operations	
8	Pickling	5-6
9	Chrome tanning	18-22
10	Washings	10-11
11	Neutralisation	5-11
12	Washings	8-10
13	Dyeing and fat liquoring	5-7
14	Washings	8-10
15	Floor washings	40-50
	TOTAL	**340-400**

Table.3 Characteristics of wastewater in mg/L

Parameter	Soaking	Liming	Delming	Pickling	Chrome tanning	Neutralisation	Dyeing
pH	7.568	12-12.8	7.1-9	2.5-4.3	3.5-4.1	4.2-6.9	3.9-4.5
Alkalinity	1150	19250	950	-	-	-	-
Acidity	-	-	-	575	4800	1050	1550
BOD	1200	1100	850	525	850	900	1650
COD	2800	23000	1900	1850	3000	4500	3900
Chlorides	6000	2850	6500	33500	10500	1250	2000
Total solids	29500	15000	7950	60500	66000	15500	19000
Suspended solids	5000	1075	2050	5000	2750	1500	1450
Sulphate	625	0.470	800	-		-	-
BOD/COD	0.428		0.447	0.283	0.283	0.200	0.423

Table.4 Daily Pollution Discharge Details

Parameters	**Total Pollutional load in kgs/day**
COD (Total)	1500-2200
COD (Soluble)	1100-1500
BOD (Total)	630-930
BOD (Soluble)	44-670
Total Solids	5900-8500
Dissolved solids	5200-7000
Suspended solids	740-1500
Chloride	1500-2400
Sulphide	20-30
Sulphate	480-780
Chromium	20-30
Phosphorus	2-7
Nitrogen	110-190
Dried sludge with 50% moisture	1600-2500
Volume wet sludge with 98-99% moisture	50-80 m^3

Table.5 Characteristics of effluent from Tannery

Parameter	Soaking	Liming	Delining	Pickling	Chrome Tanning	Neutralisation	Dyeing
pH	7.568	12-12.8	7.1 - 9.0	2.5-4.3	3.5 - 4.1	4.2 - 6.9	3.9 - 4.5
Alkalinity	1150	19250	950				
Acidity	-	-	-	575	4800	1050	1550
BOD	1200	1100	850	525	850	900	1650
COD	2800	23000	1900	1850	3000	4500	3900
Chloridies	6000	2850	6500	33500	10500	1250	2000
Total Solids	29500	28000	7950	60500	66000	15500	19000
Suspendend Solids	5000	15000	2050	5000	2750	1500	1450
Sulphate	625	1075	800				
BOD/COD	0.428	0.470	0.447	0.283	0.283	0.200	0.423

Fig.1 Flow discharge pattern of wastewater from a Typical Tanning Unit. Processing E.I to finish and wet blue to finish of producing capacity 2000Kg

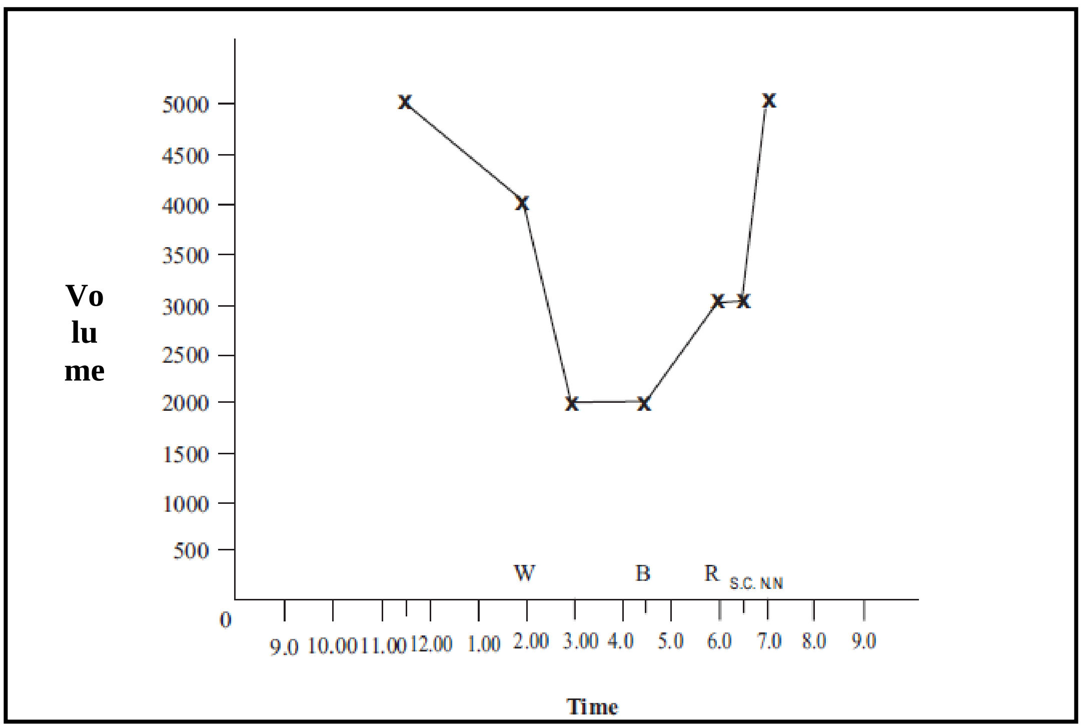
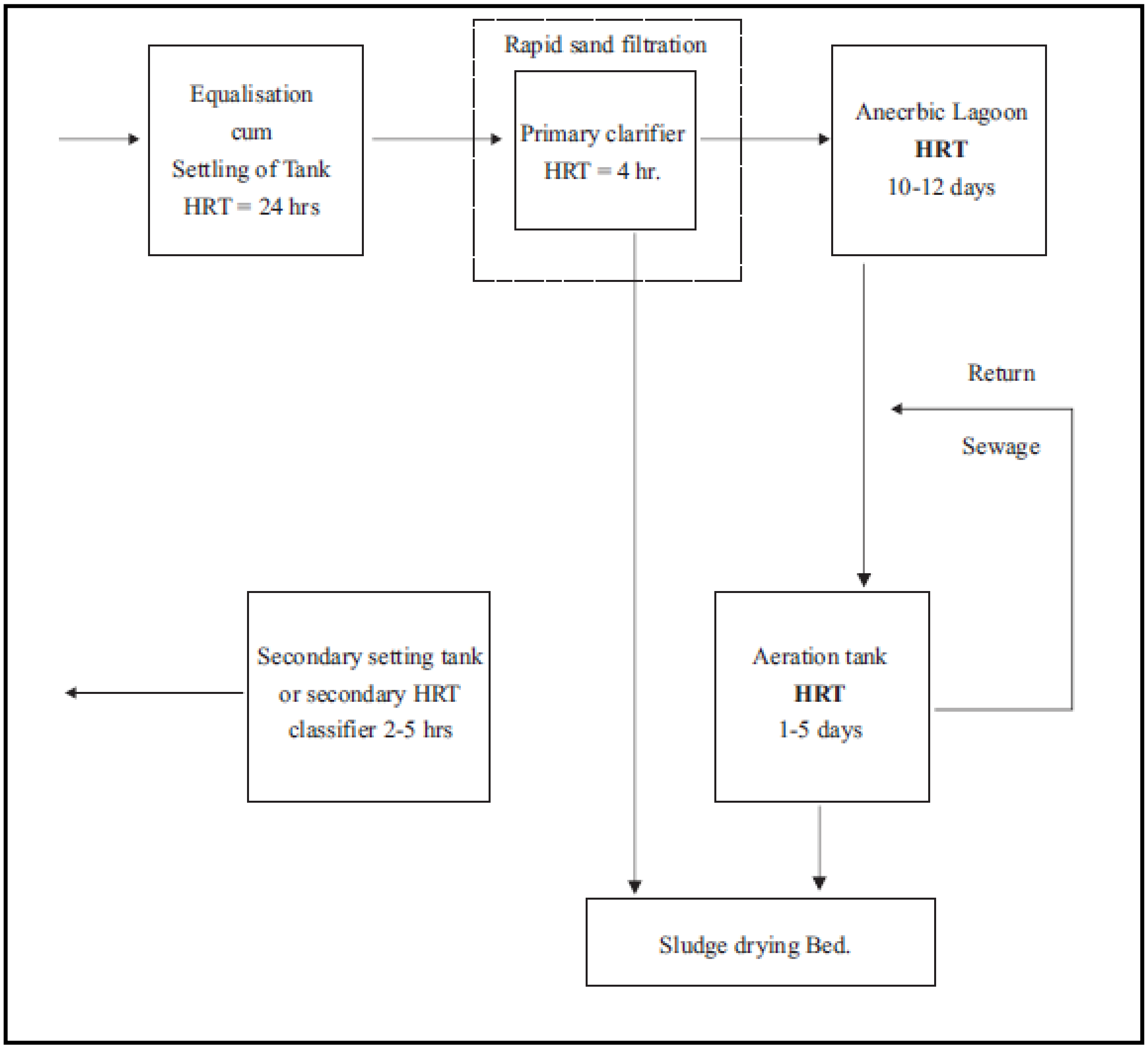


Fig.2 Schematic Diagram for Treatment of Tannery Wastewater



Equalization cum settling tank

As already pointed out that wastewater from tanning unit is discharged intermittently due to batch operations involved. Thus pH of wastewater fluctuating within a wide range, and organic load is also shifted from the average value to a greater extent. Equalisation cum settling tank is provided with the idea to equalize the strength and to maintain steady flow to the Biological treatment unit. This is done to prevent them from slow load application.

Primary Clarifier

Certain wastes like Wet blue to finish, crusts to finish are acidic in nature. Hence these wastes are adjusted to desired pH 7.8 by using lime. The pH of waste water from Raw to Wet blue and Raw to Finish are too far from 7.0. In such cases, the pH is brought to normal pH by adding alum. The calculated quantum of coagulants is mixed with wastewater, until the desired pH is reached and is flocculated at low r.p.m. Many abiotic factors can influence the rate of degradation in soil such as pH, Redox conditions and organic matter (Jensen 1996).

The detention time used for primary clarification is 24 hrs. Then the supernatant is pumped to biological treatment unit.

Biological treatment includes Anaerobic and Aerobic processes. Anaeobic treatment is used for high strength wastewaters while aerobic treatment process is used for low strength wastewaters.

(Sekaran *et al.*, 1996).Anaerobic digestion of complex organics can be described as a three-stage process –

Hydrolysis, liquefaction and fermentation
Hydrogen and acetic acid formation and
Methane formation

Hydrolysis and liquefaction are accomplished by extracellular hydrolysis for this specific purpose. It is significant to note that the stabilization of complex organic material depends upon its initial hydrolysis step. The overall rate of stabilization and methane formation can be controlled by the rate of hydrolysis of complex organics. Hydrolysis reaction of complex organic material is closely followed by formation of propionic, butyric and valic[9,10,11,12] acids. Hydrogen is produced by fermentative bacteria and acetogenic bacteria. (Wiemann, MH.Schenk and W. Hegemann,1998). Regarding methane formation the conversion of acetic acid into methane is of prime importance in waste stabilization. Acetic acid and hydrogen serve as the major substrates for methane formation in the anaerobic digestion of wastewater sludges. Major portion of methane is formed as a result of acetate cleavage.

CH_3COOH ---------> $CH_4 + CO_2$

Different anaerobic treatments are available

Anaerobic lagoon
Anaerobic contact filter (downflow and upflow)
Upflow Anaerobic Sludge Blanket (USAB)

Aerobic Process includes -Trickling filter-Rotating biological contact filter-Activated sludge process-Oxidation ditch.

The Schematic diagram shows the movement of wastewater through different units in the treatment of tannery wastewater.

About 13 % of the world's leather output comes from India. About 23 million people are employed in leather and leather related industries. In the chemical tanning process, as many as 250 chemicals are used, including heavy metals such as cadmium, arsenic and chromium.

A significant part of the chemicals used in leather processing is not actually absorbed or consumed in the process and hence it is discharged into the environment. Due to industrial enlargement, huge amounts of industrial wastes are accruing in the environment and can't be disposed (Belay, A.A., (2010). Liquid effluents from light leather processing comprises about 10 to 100 mg/L of organic matter,chromium, sulphide, and solid waste including fleshing, trimmings, shavings and, buffing dust (Cheng, Y., F. Yan, (2010). About 60% of the total chromium salts react with the hides and about 40% of the chromium amount remains in the solid and liquid wastes Lofrano, G., S, 2013. Bidut *et al.*,(2013) investigated that Cr is hazardous to human wellbeing, beasts and the surroundings. Chromium is used in large amounts and the chromium in tanning wastes spreads into the whole environment. Martin *et al.,* (1982) It is relatively immobile and insoluble substance and does not decompose but accumulates in the soil. Here chromium salts are entrained in the sludge creating serious problems for their disposal (Gauglhofer 1986). Tannery workers and people living close to tanneries experience certain specific health problems, presumably caused by contamination by the effluents. There is a high incidence of skin diseases and respiratory disorders. High abortion rates and menstrual disorders are common. Thus it can be emphasized that it would be fair to implement new cleaner technologies to reduce organics in treated waste water to trace level. Historically the tanning industry has tended to deal with new constraints by a single targeted response for (eg) compliance with chromium in effect was solved by transferring it to the sludge. Chrome recovery and reuse. (Rajamani *et al.,* 1992).

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