CHAPTER II

Literature review

Literature review :

II.I Introduction:

Tanning has been practiced from time immemorial as a craft Initially tanning was done at the village level. With the progress of time, it has gained the status of an industry playing an important role in the nation's economy Now India is one of the major leather exporters in the world and contributes about 2.5% of the world production. There are more than 3000 tanneries in different places of India and the total processing capacities of the tanneries in the country is about 700,000 tones of hides and skins per year as per 2000 estimate The total wastewater discharge from the industry has been estimated as about 90,000m^3 per day.(S. V. Srinivasan, et. al.JILTA 2004, Feb).The tanneries are mostly distributed in cluster in the states of Tamil Nadu, West Bengal, Utter Pradesh, Karnataka, Punjab and Maharastra and approximately 75% of these tanneries are in the cottage and small scale sector, 20% in the large sector Tamil Nadu alone contributes 70% of the total export of leather and leather products (Arora et al., 1972)

The leather manufacturing process involves tanning which is a chemical process converting the derma of hide/skin into a stable non-putrescible material known as leather. The basic operations to be carried out before tanning are soaking, unhairing, liming, deliming, bating and pickling etc. All these operations generate considerable amount of wastewater Table II-1 help us to estimate the nature and amount of chemicals & water used for leather manufacture and pollutants discharged from different unit operations in the tannery (Rajamoni, S.1994, 2003). Tanning is a water-consuming industry approximately 30-40 litres of water is used for processing one kg of raw hide/skin into finished leather Most of the tanneries in India are located near riverbanks or near natural water bodies to draw surface water. Some tanneries use ground water from captive open well. The quantity of water consumption and nature of wastewater discharge from tanneries depend on type of tanning process, capacity of tannery and its production pattern. The most common tanning processes are the vegetable tanning and the chrome tanning. The waste water coming out after tanning operations contains many harmful chemicals and also plenty of organic components. This water needs to be treated before discharging to natural stream. It is therefore necessary to set up effluent treatment plant. Table-II-1 gives an idea about the characteristics of tannery effluent. In India, about 100 large-scale tanneries having adequate land and managerial capacity build their own effluent treatment plant to tackle the problem of wastewater treatment. Since most of the tanneries are medium and small scale sector, the problem faced by them are manifold in nature. These units do have some limitations on available finance, land and manpower for having individual treatment plant. Lack of finance is the greatest bottleneck. To overcome these difficulties, wastewater from various tanneries in a cluster can be treated by combining the discharge from different tanneries in a Common Effluent Treatment Plant to reduce the treatment cost (Vedajnananda and Biswas, 2000). Water conservation i.e. to produce process grade water to be reused and recycled in the industry is the prime objective of the CETP. Improvement in the quality of treated effluent can be maintained by proper controlling and monitoring of the unit processes, with the use of optimum chemical dose of alum, lime, polyelectrolyte and MLSS (Mixed Liquor Suspended Solids) concentration in the aeration basin. After implementation of various measures the effluent from CETP conforming to the standards as per MEF (Ministry of Environment & Forest) except for higher chlorides and dissolved solids (Vedajnananda and Biswas, 2000). Biodegradability efficiency of dissolved solid in the aeration tank of CETP is to be increased to meet the specified standard. Though tanning industry is one of the most polluting industries, yet its pollution load can be greatly reduced by efficient effluent treatment management, optimization of process parameters etc.

Table-II-1 Characteristics of tannery wastewater :(Figures except pH are in "000s):

Tanning processes	Nature	Volume [illegible] hides	[illegible]	[illegible] Mg/l	Suspended solids Mg/l	5 day BOD mg/l	COD mg/l	Alkalinity mg/l	Chlorides mg/l
Soaking	Olive green, contains dirt, dung, blood, hair, salt etc Highly putrescible	250-400	7.2-7.5	8.0-[illegible]8	2.5-4.0	0.5-5.0	2.0-7.0	0.8-1.2	10.0-15.0
Liming	Highly alkaline, contains lime,	0.65-1.0	10-12.5	[illegible]-40	4.5-6[illegible]	5.0-8.0	10.0-20.0	2.0-3.0	1.0-1.4
Deliming	Sulphides, hair, fatty and fleshy particles in suspension	0.6-[illegible]	[illegible]	[illegible]	0.2-1[illegible] 5.0-20.0	[illegible]0-2.0	[illegible]0-3.0	0.5-1.0	0.3-0.6
Veg Tanning	Ammonium chloride, ammonium sulphate	0.3-0.4	5.0-8.2	[illegible]-40[illegible]	0.4-0.6	5.0-10.0	8.0-20.0	-	1.2-2.0
Bating	Acid odour offensive colour	[illegible]-0.2	8.[illegible]-9[illegible]		0.4-0.6	0.1-0.2	0.[illegible]-0.4	-	0.5-0.6
Pickling	Contains enzyme ammonium sulphate	0.2-0.3	3.[illegible]-4[illegible]		[illegible]3-[illegible] 0.8-[illegible]	0.5-0.8	0.5-1.0	-	2.0-2.5
Chrome Tanning	Acidic	0.4-0.[illegible]	[illegible]	[illegible]	[illegible]2-6.0	0.8-1.2	1[illegible].0-25.0		-
Dyeing, fat liquoring	Acidic, contains high conc of C[illegible] mainly Cr^{3+}	0.3-0.4	[illegible]			0.2-0.5	[illegible]0-0.6		1.0-2.0
Composite	Principal components being Colour & oily emulsions	3.0-3.5	[illegible]	[illegible]		1.5-2.5	[illegible]5-4.0	0.5-0.8	2.0-4.0

II.2 Tanning process and Characteristics of tannery effluent:

The processing of leather from raw hide/skin consists first of treating it in a succession of baths with different chemical compositions to remove all undesirable matter and secondly of endowing it with the characteristic properties of leather (putrescibility, suppleness, colour etc.). Pollution from tanneries arises thus both from the hides themselves and from incompletely absorbed chemicals.In India the tanneries generally process cow and buffalo hides, sheep and goat skins by both vegetable tanning using vegetable tan extract barks, nuts and also chrome tanning. The operations in a tannery are done in batches and discharge of wastewater is also intermittent. A brief review of different steps involved in leather making can help in understanding about the idea of the nature of chemicals and volume of water used.

Soaking- It is done with plain water to remove blood, dung, dirt etc. from hide/skin and also to remove salt. The process is carried out in pits with water, wetting agent & preservative (to control bacterial activity).The effluent from this stage contains soluble protein matter, salt and chemicals used. The volume of water used is 300-400% on the raw weight.

Liming- After soaking the material is taken to the liming yard and treated with lime as swelling agent and unhearing agent like sodium sulfide, amine, cyanide etc. in alkaline condition. The effluent of this operation therefore contains used chemicals and fatty & fleshy matter. The volume of water used in this operation is 700-1000% on the raw weight.

Deliming and Bating- In deliming operation ammonium chloride, sulphate etc., and in bating bates like trypsin a proteolytic enzyme is generally used. Therefore the effluent discharged from this operation contains those chemicals used and soluble protein as pollutant. Water consumption in this operation including washing is 700-800%.

Pickling- In this operation the pelt is treated with dilute sulphuric acid and common salt to saturate its acid binding capacity. For vegetable tanning the pelt is directly treated with vegetable tannin. In pickling operation water used is 100% on the pelt weight.

Chrome tanning- In this operation the pickled pelt is initially treated with basic chromium sulphate in the same pickling bath and then mild alkali like sodium bicarbonate is added to fix up the tanning agent. For the fixation or basification the added volume of water is 300-400% on the pelt weight.

Neutralization- The acidity of the chrome tanned leather is removed by treating the tanned stock with a dilute liquor of mild alkali like sodium bicarbonate, borax, sulphate etc., and the neutralized leather is given many washes with clean water to remove residual salts. In this operation the water consumption along with after washing goes up to about 400% on the tanned stock.

Vegetable/synthetic tanning- In this operation the delimed and bated pelt is treated with natural or synthetic acids. This process requires near 300% water and the discharged effluent contains those tanning agents, which are difficult to degrade, biologically or chemically.

Dyeing and fatliquiring- In these processes the tanned leather is coloured and then made soft and flexible by long chain aliphatic hydrocarbon. The water consumption in this process goes up to 300% on the tanned stock. The effluent, therefore, contains unabsorbed dyestuff, fatty matter along with small quantity of chromium.

Finishing- In finishing operation the water used is very small and not accountable. The brief review of the different unit operations helps us estimate the consumption of water for leather making and the most of the water used is discharged as waste.

II.3 The polluting features of tannery waste on different surfaces:

On surface water- The discharge of tannery effluent in raw state, without any treatment affects the surface water in various ways The high organic content interfering with the oxygen content of the water bodies and also, alkalinity, sulphidity, chrome content affects the aquatic life greatly Presence of lime, deliming agents, fleshings, hair etc . makes the water turbid Oily matters hinder the aeration of water surface and create an indirect effect on the survival of the aquatic life. The colouring substances and organic matters change the taste and odour ,colour etc of the water

On land- The fertility of land is affected due to the presence of sulfide and other toxic compound and has an influence on the plant metabolism. It is now recognized that the use of nitrogen bearing salts could affect the N:P:K ratios of soil Nitrogen based salts are considered a potential long-term environmental threat

On ground water- Due to disposal on land or surface water the effluent percolates through and infects the ground water

On sewers- Disposal of tannery effluent into sewers create clogging by sedimentation of lime, flashings, hair etc at the bottom of the sewers and hence chock the water flow

These various problems of tannery effluent is to be regulated by the regulation of Bureau of Indian Standards tolerance limits (BIS) through water Act, 1974 (Prevention and Pollution control) As per this legislation the concentration and tolerance limit of the different pollutants of effluent discharged in different area must not cross the prescribed limit The BIS standard limits are as given in Table II-2

II.4 Requirements of Pollution Control and Management:

According to the present Indian Environmental Pollution control regulations, the tanneries are required to set up effluent treatment plant either individually or collectively so that the treated effluent meet the pollution control standards as detailed in Table II-2. Large and medium scale tanneries with adequate land, finance and managerial capacity have set up individual effluent treatment plants.

Table- II.2. Bureau of Indian Standards tolerance limits for tannery effluents (BIS:2490.PART 3-1985):

Important characteristics	Tolerance limits for industrial effluent discharged		
	Into Inland surface waters	into public sewers	Onland for irrigation
Colour and odour	Absent		Absent
pH	6.0-9.0	6.0-9.0	6.0-9.0
Suspended solids	100	600	200
BOD 5days @ 20°C	30	350	100
COD	250		
TDS	2100	2100	2100
Chlorides	1000	1000	600
Total chromium (as Cr)	2	[illegible]	2
Hexavalent chromium (as Cr)	0.1	0.1	0.1
Sulfide (as S)	2		2
Sodium percent		60	60
Boron (as B)	2	2	2
Oil and Grease	10	20	10

Note: All values except pH and Sodium are expressed in mg/l.

Tanneries located in cluster and do not have adequate land and financial/technical capability to set up individual effluent treatment plants have jointly set up CEPT (common effluent plant treatment) system

Cluster of tanneries in cities where there is no scope even for CEPT due to non availability of adequate land, public resistance etc and scattered small scale tanneries are obliged to relocate and develop separate industrial complex with CEPT system. Indian leather sector has done exceedingly well in this regard. Nearly 70% of tanneries in India are having pollution control and treatment facilities, either individually or jointly (A Sahasranaman, JILTA, August 2002). Significant technological advancement including physico-chemical treatment followed by biological treatment and further tertiary treatment has been developed in different ETP&CETP in India to achieve higher efficiency in meeting the standards in a cost-effective manner The use of closed bioreactors offers a possibility to recover sulfer from hydrogen sulfide and energy from methane after suitable modifications Various types of tertiary treatment methodologies like activated carbon filters, reed bed and root zone techniques for removal of color, fecal bacteria and suspended particulate matters through developmental research and investigation are going on in this direction (J Raghava Rao T.Ramasami, A. Sahasranaman, et.al. ILTA, August 2001, Valedictory issue.)

II.5 Minimization of waste in Leather processing:

The tannery waste management has drawn attention and is a subject of deep concern for all concerned. Inability to comply with strict environmental regulations had resulted in closure of tanneries in some parts of the country. In combating the environmental challenges in leather processing industries, there is an attempt to emphasize excessively the importance of effluent treatment plants. The cost effectiveness of waste management in leather processing sector has remained the most important issue There is now an emerging recognition that the environmental issues in leather processing sector are better managed by an integrated eco-friendly clean technological approach. (J.Raghava Rao et.al 2001). The development and implementation of cleaner technologies in general needs i)careful audit of the emission of pollution load of every sectional stream. ii) replacement of eco-sensitive by eco-benign chemicals inputs. iii) ensuring near-total absorption of chemicals used. iv) assessment of the environmental impact of the resulting process wastes. v) inclusion of environmental costs in the overall analysis of economics and cost of products. vi) optimization of processes based on overall economic index which includes system productivity and unit value realization (Raghava Rao et.al 2001)

II.6 Cleaner leather processing:

In combating environmental challenges.the attention has now shifted from curative to preventive environmental management focussing on in-house pollution prevention and minimization i.e. reduction-recycling-recovery principles. There is an increasing recognition that treatment in isolation is not an adequate strategy to meet the requirements of wastewater norms and standards. Strategies for pollution prevention and control need to integrate cleaner process options with the better water management practices. The volume of effluent has a direct effect on the cost of treatment. The reuse of spent solutions (after removal of unwanted materials) forms an integral part of in-process control strategy and the approach of this reuse method is to target the zero or near-zero discharge of waste liquors. A variety of technology options for cleaner leather processing have emerged (J.Raghava Rao, T Ramosamy et.al 2001)

II.7 Reduction of pollutants at source:

Common salt and sodium sulfate have great contribution to pollutant in tannery wastewater. Removal of common salt and sodium sulfate is more expensive and technology-intensive. To make a more cost-effective strategy, it is better to avoid or reduce the use of such salts in leather processing. The contribution of neutral salts to tannery wastewater originates from the salts used in preservation of raw hides/skins, processing inputs by tanners and those formed during processing on account of the pH alterations employed in leather manufacture. Although there are several technological alternatives to the conventionally employed preservation methods, the utilization of such alternatives under field conditions is not popular due to several techno and socio-economic factors. However, desalting of raw hides/skins stock in tanneries has led to a reduction of 15% load of TDS (Total Dissolved Solids) at the solar pans. Enzyme assisted dehairing and use of better quality lime in tanneries have led to significant reduction in TDS load. Segregation and recycle technologies for pickle and chrome tanning liquors offer a possibility to reduce about 10% of TDS load in composite tannery wastewater. A close audit of neutral salt content of post tanning auxiliaries and appropriate choice of right formulations enable a net saving of about 5% of TDS loads in composite tannery wastewater. A typical improvement in TDS load reduction is achieved by the implementation of cleaner neutral salt saving technologies in leather sector.

II.8 Reduction of BOD&COD:

By the application of cleaner technologies in some tanneries in south India, it has been possible to reduce the BOD & COD (Chemical Oxygen Demand) loads by 30-40% per ton of leather processing. For achievement of such reduction the cleaner technologies have involved the implementation of the mechanical desalting, enzyme assisted sulfide-reduced unhairing cleaner-recycle chrome tanning. Optimization of inputs of lime, sulfide common salt and chrome tanning salt enable the reduction of BOD and COD loads through in-process changes.

II.9 Reduction of sulfide load:

Enzymatic unhairing enjoys a worldwide acceptability due to its user-friendly nature. Enzymatic unhairing can substantially reduce or even eliminate the pollution problems associated with sulphide. Enzymatic unhairing has been highlighted as an alternative to chemical unhairing and leads to significant economic environmental advantages. It has been possible to use the commercially available enzymes to replace 50-60% of sodium sulfide loads for unhairing of hides/skins. This process not only reduces pollution to a large extent, it also increases the area yield in several cases. Such increase in area could compensate for the increase in cost of enzyme assisted dehairing technology. Due to reduction of sulfide concentration, enzymatic unhairing technology save the cost of treatment of tannery wastewater by about 8-10% (JILTA,Dec 2003)

II.10 Reduction of nitrogenous salts :

Various nitrogenous salts free deliming and bating methods are gaining importance in leather manufacture. The uses of microbes or carbondioxide in deliming method are examples of such nitrogenous salts free method. Enzymes formulations free from nitrogenous salts are also in use for bating operation. The adoption of these technologies provides more than 80% reduction of nitrogen discharge from tannery wastewater. For adoption of such methods, the parameters that need special process adjustments include a) complete removal of sulfide prior to deliming, b) acidic environment instead of conventional alkaline bate and c) rigorous process control system (J.Raghava Rao, T.Ramasami, A.Sahasranaman, et.al. 2001).

II.11 Reduction of chrome:

Conventionally, basic chrome (III) sulphate is extensively used globally. Today, 80-90% of all leather is tanned with chromium salts due to its tanning potency over other tanning agents. In spite of such advantages, chrome tanning has come under severe critism due to ecotoxicological problems. It is seen that 1 ton of wet salted hide yeilds only 200 kg of leather but 600 kg of solid waste or by-product(K.T.W. Alexander, et. all JSLTC ,vol.76, p 17). Thereby, huge composite tannery effluent and solids wastes from these tannery agglomerates are discharged. An integrated chrome management has been developed and implemented which has helped to gain a significant importance in combating pollution problems emanating from chromium in tannery wastewater. It is now technologically possible and economically viable to increase the uptake of chromium during tanning to nearly 98-99% with the help of recovery/recycle methods. Chrome recovery/ recycle methods are now commercially used as mitigation methods. For high exhaustion of chrome or zero discharge closed pickle-tan loop methods have emerged based on polyamides, protein hydrolysates, polycarboxylic acids and other organic additives have been introduced in cleaner chrome tanning as a mitigation methodology. These mitigation methods are eco-benign and cost effective. Saving in post tanning materials has been observed in many tanneries in the country. It has been seen that there is a net saving of Rs.2000 - per ton of leather processed (J.Raghova Rao, et. all 2001).Practically this technology helps to eliminate the problem offered by chromium based tanning methods.

II.12 Bioremediation :

Technologies have been developed for replacement of eco-constrained chemical inputs. Numbers of technology options for short-term preservation have already been developed. Since, common salt used for preservation has been one of the most environmentally disconcerting discharges; alternatives to common salt as a medium for preservation have formed the focus area of research. For salt-free short-term preservation the idea of using Lactobacillus culture has been developed in a similar way as had been in use for food preservation (carbohydrates are digested to form lactic acid and the resulting acid medium could be expected to suppress the growth of most bacterial cultures as well as yeasts and many moulds,pH 3.5 – 4.5), (C.S.Cantera, JSLTC, Vol.85,p-125).Bio-unhairing means the unhairing process with a bacteria culture. The bacterial population of an enzyme unhairing liquor is the result of the growth of organisms added with the hide, the water and the enzyme.The viable bacteria supply a heavy inoculum to the unhairing liquors, the cells present in the preparations containing a high number of bacteria are found to be mostly in the spore form. Under the conditions used for unhairing (24h, 300c), the spores germinated in a few hours and built up to about 300 million bacteria per ml within 24hrs. The contributions of bacterial growth help to the depilatory action of the liquor (Cordon et al.). Schlosser et al. developed a novel method of depilation of cattle hides in an acid medium by using a certain Lactobacillus culture. It has been possible to remove chromium from effluent by bacterial strain NCIM 5080 &NCIM 5109. The strain has been identified by the collaborative activity of scientists of NCL (National Chemical Laboratory, Pune) and CLRI (Central Leather Research Institute, chennai). Two novel strains of actinomycetes can, in just one day, eat away all the chromium present in effluent.