INTRODUCTION

Tanneries convert animals hide and skin into leather through various processes. The raw material for the leather industry is the waste product from the slaughter house. It is the by-product of meat industry. The waste water discharged from the industries are major issue in Indian states such as Tamil Nadu (Buljan, 2005). The importance of environmental standards in India’s export was first experienced when Germany, one of the major importers of leather and leather goods from India, banned the import of leather products containing more than 5 mg/kg of pentachlophenol (PCP) in 1990 (Chandan Roy, 2012). This was followed by a German ban on the import of leather and textiles treated with a number of azo dyes in 1994 (Catherine Money, 2005). Environmental aspects been taken into consideration from 1990’s. Effluent Treatment plants were set up in early 1990’s and the effluent treated by conventional method (Sahasranaman and Sampath Kumar, 2001). In India the major clusters of tanning industries are Ambur, Vaniyambadi, Pallavaram, Pernambut, Ranipet, Dindigul and Trichy in Tamil Nadu and Kanpur in Uttar Pradesh, Kolkata in West Bengal and Jalender in Punjab (Sahasranaman, 2002). Around 45% of the total tanneries in India are located at Tamil Nadu. In Tamil Nadu the major tannery clusters are located at Vellore District (Kavitha and Ganapathy, 2015). The tanning industries were operated without and partial pollution control for more than 10 decades. Only after 1980 the treatment of the tannery wastewater was carried out (Buljan and Kral, 2011). The waste water discharged from the industries were partially treated by conventional method and let out to Palar River which results in ground water pollution (TNPCB, 2010). There is no flow in the Palar River due to the failure of monsoon for the past fifteen years and the construction of reservoirs in the upstream of the river. The ground water table decreased due to the continuous withdrawal of water for the agricultural, industrial and domestic uses (CPCB, 2000). Further the continuous discharge of effluent leads to the increase of dissolved solids in the ground water and drastic increase of dissolved solids emerged the need of advanced wastewater treatment.

2. STUDY AREA

About 630 tanneries are located at various clusters at Vaniyambadi, Ambur, Ranipet, Pernambut in the area of about 1650 sq.km. Vellore is located at the bank of Palar river with population of 5, 01,966 (2011). Around 40% of the leather export of our country is from Vellore District. Vellore district has an area of 6077 sq.km and is one of the 31 districts in the Tamil Nadu state of India. Vellore is the headquarters of this district. It lies between 12º15’ to 13º15’ North latitudes and 78º 20’ to 79º 50’ East longitudes in South Indian state, Tamil Nadu. Palar River is one of the major water sources running west to East located at downstream of the industrial complex.
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Figure 1. Location map of the study area

2.1. Approach: There are three major type of leather process carried out namely Raw to finish, Raw to semi finish and semifinish to finish with two type of tanning called vegetable tanning and chrome tanning. The major raw materials for these tanneries are hides of cow and buffalo and skins of sheep and goat. The different stages of leather processing and waste generation are depicted as flow diagram in Figure 2.

Figure 2. Stages of leather processing and waste generation

2.2. Leather process: Preservation of hides and skins is the first process in the leather making. Drying of skins and hides, cooling and chilling are carried out to preserve the hides and skins. The hides and skins should be preserved from the microbial attack and putrefaction. The microorganisms secrete proteolytic enzymes and

(Figure 1). Vellore district has the major tannery clusters in Tamil Nadu. Out of 14 Common Effluent Treatment Plants (CETPs) in Tamil Nadu for tannery effluent, 10 CETPs are located at Vellore district.
hydrolyze the hides/skins and make them unsuitable for leather manufacture. The procedure to prevent bacterial attack on hide/skin is called as Curing. There are basically three major steps- Pretanning, Tanning and Post Tanning involved in leather making, with many processes in each step (David Pearce and Hayden Fisher, 2009).

2.3. Pretanning processes: Soaking, liming, de liming & Bating. Pickling and degreasing are some processes in the first stage (Krishnamurthy, 1977). In the soaking process, the cured skin/hide are soaked in water to rehydrate their original flayed condition and to remove the dirt, flesh, hair and some soluble proteins like albumin and globulin (Aravindan, 2007). Paddles or pits are used for soaking and by every stage 200 – 400% of water by weight of the skin or hide is soaked. 0.1% biocides (preservative) and 0.2% detergent (wetting agent) are added at the first step and a considerable volume of salt and impurities carried out through soak liquor (Sharphouse, 1989). In the liming process, to loosen the hair, the soaked hides and skins are treated with a mixture of lime and sodium sulphide in pits or paddles and it is called unhairing (Rajamani, 1998). Next reliming carried out where the unhaired hides and skins are again treated with soda ash or sodium hydroxide for the opening of fibre structure and flesh loosening. The unhaired and flesched hides are called pelts. Deliming is carried out to remove the alkalinity caused by lime on the collagen (Jakov Buljan, 2001). Pelts are treated with mild acids like acetic acid, boric acid, lactic acid or acid salts like ammonium sulphate, ammonium chloride or sodium bisulphite to remove excess alkali. Then it is bated using bating agents to remove interfibrillary proteins and to get a clean white pelt. Skins used for gloving and plating and embossing.

drying system or by curtain coating machine, the finishes are applied. The final finished leather is called crust. Depending upon the customer's need and the condition of the leather, the finishing is carried out (Kanagaraj and Chandra Babu, 2002). In suede leather, buffing is carried out to remove nap fibers.

2.4. Tanning Process: Tanning process converts the putrescible hide or skin to non-putrescible and durable product. Tanning is the reaction between the collagen and chemical. It gives resistance to bacteria, enzymes and hydrolysis. It imparts hydrothermal stability. The three major types of tanning are Vegetable tanning, Chrome tanning and combined tanning. The two kinds of tanning agents are organic tanning agents and mineral tanning agents. The salts of chromium, aluminium and zirconium are the mineral tanning agents. Tanning agents like formaldehyde, fish oil, calgon and silica are used in the production of certain types of leathers. Excess water and wrinkles are removed by a process called Sammying. Then it is split into uniform thickness followed by dyeing in drums. Depending upon the leather quality requirement, the quantity and quality of the dye differs. Depending upon the acidity, dye bath temperature, tannage type, drum speed, float, dye concentration and special additives, the penetration, shade richness and dry cleaning varies in the dyeing. Leather drying prevented by proper lubrication. Oils and fats are treated with the leathers for the softness, lubrication, waterproof, and strength. These oils and fats are blended with the leather in the drum. Oil is swabbed on the grain surface of the vegetable tanned light leathers. A mixture of mineral oil, vegetable oil, sulphated oil, glucose and Epsom salt are applied for the sole leathers. The light colored, supple leather are produced by using the oil which keeps the tanning material loose from raising the grain during drying. A mixture of cod oil, tallow, wool grease, paraffin wax is treated with belting leathers (John Sundar, 2005). Fat liquoring of light leathers are carried out in an oil-water emulsion. Along with a solvent, the oil is introduced into the leather and the solvent is been evaporated. Leather contains 45 – 60% water after dyeing and fat liquoring and dried to 14% moisture. During drying process, the loose tannins, dyes and oils penetrate uniformly and deeply into the leather and fixed firmly. Uneven drying leads to migration of unfixed tannin dyes and oil to the surface and dark stains in loose areas occurs. Leather tends to shrink during the drying process and the drying temperatures are high. The shrinkage will be low in vegetable tanned leather.

2.5. Post Tanning Processes: The uniform thickness, softness, gloss etc are obtained during the post tanning operation. The dried leather is trimmed, conditioned with saw dust to get uniform moisture content and staked over a steel blade to stretch and soften it. The finished leather after this process is called crust. To improve the surface properties of the leather and to increase the aesthetic properties, the finishing is carried out (Kanagaraj and Chandra Babu, 2002). In suede leather, buffing is carried out to remove nap fibers.

2.6. Finishing: The finishing stage of the leather is the coating on the grain surface. Two types of finishing carried out. Glazed type and Resin finished leather. Pigment paste colors or simple dye colors are used for the leather coloring. Varieties of pigments, resins, binders and waxes are used for finishing. Binders like casein and shellac, synthetic resins are used for mat finish. The surface defects are covered by pigment finishes. Organic pigment in emulsion is applied in aniline finish with very little loading and leathers are finished with natural look (Covington, 1997). The steps involved in finishing are clearing coat, sealing coat, impregnation, base coat, season coat, effect coat. Depending upon the customer’s need and the condition of the crust leathers, the required steps are followed in finishing. Using auto spraying machine with conveyor drying system or roller coating machine with conveyor drying system or by curtain coating machine, the finishes are applied. The final finished leather obtained after ironing, plating and embossing.
3. RESULTS & DISCUSSIONS

3.1. Environmental impact of leather processes: The leather industries are the major industries on the basis of international trade and it has economic significance. The criticism continues on these industries on the basis of environmental impact and this industry is being described as the major source of water pollution. The tannery effluent consists of pollutants like protein, hair, salt, lime, sludge and sulphides. The groundwater near the tanneries is highly polluted over a period. Farmers complain the infertility in their land due to the dumping of tannery waste and tannery effluent (Jan Tiest Pelckmans and Campbell, 2010). The high environmental impact of leather processes is mainly due to the high use of chemicals in the process (Ramasami, 2007) and letting it out in the effluent causing soil and water pollution, air pollution during dehairing, letting out hydrogen sulfide and during deliming, ammonia let outs and solvent vapors and slow biodegradability (Ganesh Babu, 2007). Cleaner tanning technologies reduce the pollution load by the usage of quality chemicals with optimum dosing and water conservation during the processes (Balachandran, 2006). The tanning industries are now come up with advanced technologies to treat the wastewater and taking back the treated water for the reuse in their processes and salt recovery from the concentrated waste (Preethi, 2006) and thus reduce the impact on the environment (Govindasamy, 2006).

3.2. Analysis: The water consumption for the production of leather from one tone of raw hides is around 15000 to 40000 litres and 110 to 260 liters per sheepskin (Ashact, 2000). This will produce around 20 - 80 % of effluent with 100 – 400 ppm chromium, 200-800ppm sulfide, fat, solid wastes and pathogen contamination (Bosinic, 2000). Pesticides added for the hide conservation during transport is also cause pollution. Figure 3 shows the volume of water used in the various leather processes and volume of wastewater discharged after the process of hides and skins. The volume of water consumption and the wastewater discharged is expressed in liter per kilogram.

![Figure 3. Water consumption and wastewater production in various types of leather processes](image)

3.3. Solid waste from tanneries: The tannery processes contribute pollution load in the form of solid waste from various processes (Daniels, 2005). Raw trimmings of 80-120 kg/T, 40-50 kg/T of hair/wool, 250 – 300 kg/T of fleshing, 100 – 110 kg/T of wet blue trimmings, 90 – 120 kg/T of wet blue shavings, 6-8 kg/T of crust trimming, 1-2kg/T of buffing dust generated from the raw material (Valentine Post, 2003). The characteristics of the tannery effluent in various processes been tabulated in the Table 1.

3.4. Improvements in the last three decades in the production and export: The improvement of leather industry in India for the past 5 decades is significant. The data on improvement of the industry in the past three decades is shown in the Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Soaking</th>
<th>Liming/reliming</th>
<th>Deliming</th>
<th>Pickling</th>
<th>Chrome tanning</th>
<th>Neutralisation</th>
<th>Recchroming, Fat liquor</th>
<th>Total (including washings)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of effluent/ton of hide/skins</td>
<td>6-9 m³</td>
<td>3-5 m³</td>
<td>1.5-1 m³</td>
<td>0.5-1 m³</td>
<td>1-2 m³</td>
<td>2-3 m³</td>
<td>3-6 m³</td>
<td>30-40 m³</td>
</tr>
<tr>
<td>PH</td>
<td>7.5 – 8.0</td>
<td>10.0-12.8</td>
<td>7.0-9.0</td>
<td>2.0-3.0</td>
<td>2.5-4.0</td>
<td>4.0-6.5</td>
<td>3.5-4.5</td>
<td>7.0-9.0</td>
</tr>
<tr>
<td>BOD 5 day at 20°C (Total)</td>
<td>1,100-2,500</td>
<td>5,000-10,000</td>
<td>1,000-3,000</td>
<td>400-700</td>
<td>350-800</td>
<td>800-1100</td>
<td>1000-2000</td>
<td>1200-3000</td>
</tr>
<tr>
<td>COD (Total)</td>
<td>3,000-6,000</td>
<td>10,000-25,000</td>
<td>2,500-7,000</td>
<td>1000-3000</td>
<td>1000-2500</td>
<td>2000-4500</td>
<td>2500-7000</td>
<td>2500-8000</td>
</tr>
<tr>
<td>Sulphides (as S)</td>
<td>-</td>
<td>200-500</td>
<td>30-60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30-150</td>
</tr>
</tbody>
</table>
The leather industries had become an important source of employment and foreign exchange for the country. The organic and chemical pollutants from the conventional leather process are high and discharged through the effluent which causes serious threat to the soil and water bodies. Environmental concerns are increased by the preference given for the leather produced by cleaner technology in the country. The organic and chemical pollutants from the conventional leather process are high and discharged through the effluent which causes serious threat to the soil and water bodies.

Table 2. Leather industry improvement in India (Value in million rupees)

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Value of production</td>
<td>3,000</td>
<td>59,570</td>
<td>110,560</td>
<td>160,000</td>
<td>2,80,000</td>
</tr>
<tr>
<td>Export</td>
<td>1,830</td>
<td>32,170</td>
<td>69,560</td>
<td>92,120</td>
<td>2,33,323</td>
</tr>
<tr>
<td>Domestic consumption</td>
<td>1,170</td>
<td>27,400</td>
<td>41,000</td>
<td>67,880</td>
<td>92,320</td>
</tr>
</tbody>
</table>

Note: 1. Export figures based on actual, (Source: Council for Leather Exports)
2. Domestic consumption figures, estimated

4. CONCLUSION

The leather industries had become an important source of employment and foreign exchange for the country. The organic and chemical pollutants from the conventional leather process are high and discharged through the effluent which causes serious threat to the soil and water bodies. Environmental concerns are increased by the preference given for the leather produced by cleaner technologies. Environmental pollution awareness started in 1990’s and gradually the pollution level getting decreased by the technological application of treating the effluent.

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REFERENCES


Balachandran unni Nair, Jonnalagadda Raghava Rao, Palanisamy Thanikaivelan, Subramani saravanabhavan, Thiirnalachari Ramasami, Reversing the conventional leather processing sequence for cleaner leather production, Environmental Science Technology, 40(3), 2006, 1069-75.


CPCB, Technology alternatives for tanneries industry in India, Central Pollution Control Board Report, 2000.

Chandan Roy, A study on Environmental compliance of Indian Leather Industry & its far-reaching impact on leather exports, Munich Personal RePEc Archive: XLVII, 2012, 3-36.

Catherine Money, Salinity reduction in tannery effluents in India and Australia, Australian Centre for International Agricultural Research, 2005, 12-24.


Jakov Buljan, Solomon Sampathkumar, Viswanathan M, Desalting of Raw hides/skins and reuse of used salt in the pickling operation, United Nation Industrial Development Organization, Industrial sectors and Enviroment, 2001, 6-16


Tamil Nadu Pollution Control Board, Revised action plan for critically polluted area, Ranipet, TNPCB, 2010, 14-30