ABSTRACT

In the leather sector different types of finished leather is prepared from salted raw skins. There are about 596 tanneries in Pakistan in the formal sector and more than 90% of their product is exported. About 130 different types of chemicals are used in leather manufacturing which ranges from common salt (Sodium Chloride) to very expensive Chrome Sulphate. The chrome tanning process is widely employed in Pakistan. Many chemicals are used to prepare hides for tanning and after performing their function these chemicals find their way into the environment. All three categories of waste, i.e. gaseous, liquid, and solid are generated from the tanneries.

The paper aims to address the environmental pollution problems in the leather-manufacturing sector of Pakistan. It is based on findings of Environmental Audit of 4 tanneries carried out by Federation of Pakistan Chambers of Commerce and Industry in Pakistan under Environmental Technology Program for Industry (ETPI) Project. Based on this environmental audit an effort has been made to assess the nature and extent of the environmental problems and to develop solutions for tanning industry in Pakistani context. The paper gives an overview about the environmental issues of tanneries along with possible cost-effective remedies including recycling of different wastes to solve these problems. This study is aimed at helping the local tanneries to comply with National Environmental Quality Standards (NEQS), forthcoming ISO14000, and to enable them to produce environmentally clean product.

LEATHER INDUSTRY IN PAKISTAN

There are about 596 tanneries in Pakistan in the formal sector and more than 90% of their product is exported. Leather production uses raw material in the form of cow and buffalo hides and goat and sheep skins and a number of imported chemicals. The raw material is locally collected. About 130 different types of chemicals are used in leather manufacturing which ranges from common salt (sodium chloride) to very expensive Chrome Sulphate. Leather manufacturing involves following major steps:

1. Pre-Process
2. Pre-Tanning Process
3. Tanning Processes
4. Wet Finishing Process
5. Dry Machining
6. Finishing

In pre-processing skins/hides are received and salt is applied on the flesh side of the skins/hides. Skin trimming is done to remove unwanted parts. After pre-processing, pre-tanning process starts with the soaking process in which skin are made flaccid by soaking them in water. After soaking hair are removed,
lime is used to make hair loose. Unwanted flesh is removed with the help of fleshing machines after liming process. To prepare limed skin for tanning, the skins are delimed using Ammonium Sulphate and then skins are washed. Bating is done for further purification of hide. After that degreasing is done with the help of detergents. Tanning process starts with pickling which is the treatment of skin with acids and salts to bring it to desired level of pH. Tanning may be defined as the treatment of skin for preservation. Chrome tanning uses Chromium Sulphate as tanning agent. Tanning process stabilize the collagen network of skin. After tanning skins are called wet blue and are stored for sometime and then they are sorted out according to quality. If hides of cows or buffaloes are being used for leather manufacturing, then after this they are sliced to give desired thickness. This process is not carried out on the skins of goats or sheep. After this the hair side of the wet blue are shaved to give the desired thickness.

In order to give desired softness, color, strength, and quality to the leather wet blue skins are processed further through wet finishing process. Fat liquoring process is carried out to impart desired softness and dyeing is to give it a color. After wet process different drying processes are carried out to dry the processed leather. These processes consist of smaying/setting, vacuum drying, stacking/toggling, buffing/shaving, trimming, pressing, and segregation of the leather. Finally finishing processes are carried out to impart durability and beauty to the leather. The chemicals used in the leather industry can be divided into three broad categories:

1. Pre-tanning Chemicals
2. Tanning Chemicals
3. Finishing Chemicals

Pre-tanning chemicals are used to clean and prepare skins for the tanning process and they are mostly washed away with the wastewater. Tanning chemicals react with the collagen fibers of the skin to convert them into leather. These chemicals are retained in the skin but a good amount of these is discharged into wastewater. Chrome Sulphate is the basic tanning chemical. Apart from being expensive, Chrome Sulphate is also a serious pollutant. Finishing chemicals are used to impart certain properties to the leather like softness, color, appearance etc. Like tanning chemicals finishing chemical also get discharged into wastewater. Only those chemicals are fully retained which are applied as surface coating. A large amount of water is used in whole manufacturing process. The collected data shows 50-150 liter water is used for conversion of one kg of raw skin into leather. In tanning process water is used as carrier to facilitate different chemical reactions and after completion of process the water leaves the system as wastewater in the same quantity as added to the system. Ground water is mainly used as processing water.

POLLUTANTS
All the three categories of waste solid, liquid, and gaseous, are emitted by the leather industry in the form of:
1. Wastewater
2. Solid Wastes
3. Air Emissions

The results of environmental auditing are described below:

Wastewater
Water is used as the carrier for chemicals to render the cleaning of raw hides and skins. The water after completion of the process is drained out in the same quantity as it was used in the process. Normally water consumption of 50 liter/kg is recommended for tanneries but it is found that tanneries generally consume
more water and in some cases it is found to be as high as 150 liter/kg. Samples of water were taken from different processes of leather manufacturing and were analyzed. Tannery wastewater is highly polluted in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, total Kjeldhal Nitrogen, conductivity, Sulphate, Sulphide, and Chromium. The quantity of these pollutants in the water is very high as compared to the quantities mentioned in the NEQS (National Environmental Quality Standards) set by the government of Pakistan. Considerable quantity of sludge is also found in the waster water.

Wastewater of each tannery process consists of pollution of varying pH values. Similarly a large variation exists in every parameter BOD, COD, Chloride, Sulphate, etc. Discharge of these chemicals into wastewater is hazardous for the environment. Tannery’s wastewater is highly contaminated and the contamination observed is many times beyond the limits set by Environmental Quality Standards for all wastewater parameters. A comparison of average quantities of Pollutants from Tanneries with NEQS is shown in Table –1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>* Raw sheep &amp; goat skin-finished leather mg/l</th>
<th>** Raw calf hides-finished leather mg/l</th>
<th>*** Wet blue (goat &amp; sheep)- finished leather mg/l</th>
<th>NEQS Mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>9.33-9.88</td>
<td>7.35-7.67</td>
<td>3.52-3.55</td>
<td>6-10</td>
</tr>
<tr>
<td>BODs (Unfilled) at 60 minutes settling</td>
<td>11050-14827</td>
<td>840-1740</td>
<td>714-1346</td>
<td>80</td>
</tr>
<tr>
<td>COD (Unfiltered) at 60 minutes Settling</td>
<td>41300-43000</td>
<td>1000-2680</td>
<td>2000-3500</td>
<td>150</td>
</tr>
<tr>
<td>Suspended Solid at 0 time settling</td>
<td>4270-4650</td>
<td>820-1920</td>
<td>1970-6620</td>
<td>150</td>
</tr>
<tr>
<td>Sulphate as SO\textsubscript{4} at 0 time settling</td>
<td>1814-3146</td>
<td>800-860</td>
<td>5480-6480</td>
<td>600</td>
</tr>
<tr>
<td>Sulphate as (S) at 0 time settling</td>
<td>288-292</td>
<td>1.2-2.6</td>
<td>Nil</td>
<td>1.0</td>
</tr>
<tr>
<td>Chromium (Cr) at 0 time settling</td>
<td>64.133.3</td>
<td>41</td>
<td>160-194</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Quantity of Raw material: 12000 kg/day
Volume of wastewater : 600 m\textsuperscript{3}/day

** Quantity of Raw material: 5500 kg/day
Volume of wastewater : 814 m\textsuperscript{3}/day

*** Quantity of Raw material: 10000 kg/day
Volume of wastewater : 110 m\textsuperscript{3}/day

Source: ETPI Survey

**Solid Wastes**

The major solid wastes consist of dusted curing salt, wet trimmings, dry trimmings, wet shaving, buffing, etc. These wastes are generally separated at the source. During handling of raw skins, adhered dusted salt, which is contaminated with blood, hair, dirt and certain type of bacteria is removed and dumped. Trimmings are cuttings of edges of raw skins. Fleshing is the flesh material of the limed skins generated during fleshing operation. Chrome wet shaving is produced when skins are shaved for proper thickness after chrome tanning.

Except dusted salt most of the solid wastes are sold in the local market to the poultry feed manufacturers due to the protein content of the solid wastes. The main problem with these wastes is their high Chromium
content. The Chrome tanned waste contains Chromium in trivalent form but it was found that when the solid wastes are used in making poultry feed the Chromium is converted to hexavalent form which is carcinogenic. The mixing of this metal in poultry feed could produce serious human health problems. It is estimated that for a tannery producing on an average 10,000 kilograms of skins per day, a total of about 5,500 kilograms of solid waste would be produced per day. Table 2 presents a breakdown on this waste and its key characteristics with comments.

**Table 2: Solid Waste in Tanneries**

<table>
<thead>
<tr>
<th>Type of Solid Waste</th>
<th>Rate of Generation</th>
<th>Characteristics of Solid Waste</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dusted Salt</td>
<td>0.1 kg/skin</td>
<td>Contains around 120 gm/kg of moisture, 120 gm/kg of volatile matter, 450 gm/kg of salt.</td>
<td>Contaminated with blood, hair, dirt and bacteria. Partly reused in curing and the rest is indiscriminately dumped in undeveloped lands near the tanneries.</td>
</tr>
<tr>
<td>Raw Trimmings</td>
<td>0.024 kg/skin</td>
<td>Proteins</td>
<td>The skins are trimmed (especially at legs, belly, neck, and tail parts) in order to give them a smooth shape. The trimmings are usually sold to soap and poultry feed production.</td>
</tr>
<tr>
<td>Fleshing</td>
<td>0.25 kg/skin</td>
<td>Contains around 240 gm/kg of proteins, 200 gm/kg of fats, 3 gm/kg of sulphide.</td>
<td>This is the flesh material of limed skins. It is usually sold to soap and poultry feed makers.</td>
</tr>
<tr>
<td>Wet Trimming/ Wet shaving</td>
<td>0.14 kg/skin</td>
<td>Contains around 240 gm/kg of proteins, 30 gm/kg of fats, 15 gm/kg of chromium oxide</td>
<td>After chrome tanning, skins or split hides are shaved to proper thickness. This operation produces solid waste containing chrome. Secondary users including poultry feed makers, usually collect these shaving from the tanners.</td>
</tr>
<tr>
<td>Dry Trimmings/ Dry Shaving/Buffing Dust</td>
<td>0.06 kg/skin</td>
<td>Contains around 300 gm/kg of proteins, 130 gm/kg of fats, 30 gm/kg of chromium oxide</td>
<td>Secondary users, including poultry feed makers, collect cuttings and dry trimmings and buffing dust of the leather from the tanneries.</td>
</tr>
<tr>
<td>Assorted Refuse</td>
<td>No consistent quantity</td>
<td>Primarily cartons, bags, drums, etc.</td>
<td>This is normally sold separately (in bulk) in the retail market.</td>
</tr>
</tbody>
</table>

Source: ETPI Survey

**Air Emissions**

In tanneries air emissions are produced from the stacks of boilers and generators and during the processing of leather. Emissions from the stacks are well within the limits and pose no serious environmental impact. But hydrogen Sulphide and ammonia gases which are emitted during different processes are a health hazard for the workers.

**ENVIRONMENTAL IMPACTS OF POLLUTANTS**

Out of the three wastes mentioned, air emissions are very low as compared to the standards mentioned in NEQS whereas the solid wastes are used in preparation of poultry feed which pose health problems. The wastewater is a serious threat to the environment. Tanneries are disposing of their wastewater into drains, which finally find its way into natural water bodies. Therefore major environmental problems are linked with the wastewater of tanneries.

The pH of directly discharged tannery effluent varies between 3.5 to 13.5. Water with a low pH is corrosive to water-carrying systems and can lead to metal dissolving in the water. The high pH water can cause scaling in the sewers. Also large fluctuation in the pH value is detrimental to some aquatic species. The large quantities of proteins and their degrading products forming a major part of the wastewater can
effect Biochemical Oxygen Demand (BOD). The high value of BOD in extreme cases can kill natural life in the affected area. Tanneries discharge water having 10-190 times the recommended value of BOD by NEQS. Chemical Oxygen Demand (COD) value in wastewater is in a range of 1000-43000 mg/liter which is 25-275 times more than the NEQS standard. Sulphide in the wastewater releases hydrogen Sulphide gas which has an objectionable smell even in trace amounts. It is highly toxic for many forms of life. In higher concentrations fish mortality may also occur. NEQS recommends a value of 1g/liter for Sulphide where as tanneries' wastewater contains 290mg/liter.

Trivalent chromium is released from chrome tanning process. This is much less toxic than Hexavalent Chromium. For plants and animals the toxicity of chromium is variable. Algae have been shown to very sensitive to the chromium levels. At present tanneries are discharging chromium 133mg/liter whereas NEQS standards recommend a value of 1mg/liter. Suspended solids discharged in the wastewater forms a layer on the bottom of watercourse and covers natural fauna on which aquatic life depends. This can lead to localized depletion of oxygen supplies in the bottom waters. Suspended solids also reduces light penetration and thus photosynthesis in the water. Apart from these Sulphate and natural salt is also found in the wastewater. This can effect fresh water aquatic life if their concentration becomes too high. There is no economic way of removing them.

Poultry feed manufacturers collect these materials from tanneries and use it due to the protein content of the solid wastes e.g. fleshing, raw trimming, chrome shaving, buffing dusts etc. These wastes contain chrome in the range of 14-26 gm/kg. Chromium in the waste is in trivalent form which is less toxic than hexvalent form. A recent survey under Pakistan Tanneries Association showed that poultry feed made using solid wastes contain hexvalent form of chromium also. It seems that during feed preparation the transition of trivalent chromium to hexvalent chromium takes place. This pose a serious threat to human health.

REMEDIAL MEASURES
Several remedial measures are suggested to lessen the environmental impact of tanneries. In large and medium sized tanneries environmental management system must be developed. Staff should be trained for occupational health and safety. Gaseous masks must be provided for workers in order to prevent inhalation of fumes. Proper arrangement must be made to stop use of tanneries solid waste to make poultry feed. Improvement in drainage system is needed to avoid the formation of hydrogen Sulphide in the tannery. Many options are available for reuse of chrome, discharged in the tanning effluent. This includes direct recycling of chrome tanning float, recycling of chrome after precipitation, and use of tanning products that improve the exhaustion rate. One feasibility study shows that in conventional chrome tanning process 25-30% chromium goes into wastewater. The recovery cost of this is only 30% of the chromium recovered, hence the entire system has a payback period of less than a year.

Wastewater should be treated at two levels: primary and secondary. Primary treatment is consists of mechanical screening, pH leveling, coagulation and flocculation, and sedimentation. Secondary treatment uses biological processes to remove most of the organic matter form the wastewater. For secondary treatment of wastewater of tanneries many treatment technologies are available like activated sludge, percolating filter, aerated lagoon, facultative lagoon etc. However considering the organic and hydraulic load of the tanneries it is inferred that activated sludge treatment is best suited for secondary treatment. In activated sludge treatment the wastewater is introduced in a tank aerated by mechanical stirring or by compressed air. After sufficient contact time the mixture is clarified in settling pond and sludge is recycled
in the aeration tank. The excess sludge from the system is treated with the primary sludge. This is a
proven technology for the treatment of tannery wastewater world-wide and widely used all over the world.

RECOMMENDATIONS
The above study shows the harmful effect of numerous chemicals generated by the leather industry. Chemical
recovery and reuse is an economically feasible alternative for the leather sector. With their short payback period
chemical recovery plants are financially attractive options. Leather industry should make all attempts to reduce
its impact on environment by making every effort to reuse and recycle chemical compounds. Following steps
may help in making the leather industry environmentally friendly.

1. Training programs on occupational health and safety and modern practices of handling chemicals should
   be conducted.
2. Information about safety, health and environment should be displayed in the tanneries.
3. Use of safety items such as face protective shields, acid resistant gloves, aprons, masks may be strictly
   enforced.
4. Sequential washing instead of continuous washing may be used to conserve water. This will lead to
   significant water saving and to a much reduced hydraulic load for the effluent treatment plant.
5. Environmental friendly chemicals may be used e.g. replacing sulfides and surfactants with enzymatic
   products.
6. Avoid the formation of hydrogen sulfides inside the tanneries by improving the drainage system.
7. Proper action should be taken to stop the use of tanned solid wastes in the preparation of poultry feed.
8. Chemical recycling should be practiced.

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