Responding to the Environmental Challenge

Pakistan's Leather Industry

Profile
Pakistan's leather industry is one of the major foreign exchange earners for the country. About 90% of its products are exported in finished form. During 1996-97, the production of leather was about 14.3 million m² and export earning amounted to US$ 642 million. There are some 600 tanneries in the formal sector and an equally large number of tanneries in the informal sector. These are concentrated in a few clusters of which Kasur (180 tanneries), Karachi (170), and Sialkot (135) are the most important.

Animal skins—which are the basis of the leather industry—are obtained from the provinces of the Punjab and Sindh. Limited quantities of imported hides are also used. The season of peak activity begins around Eid-ul-Azha and extends for between two to three months. During this period, production levels can reach twice the normal level.

The chrome tanning method is the most widely used process in Pakistan's leather sector. However, the vegetable tanning method and a combination of chrome and vegetable tanning is also applied. The process includes a number of different steps during which large quantities of water and chemicals are applied to the skins. About 130 different chemicals are used in leather processing, depending on the type of raw material used and finished product. These may be divided into four major classes: pretanning chemicals, tanning chemicals, wet finishing chemicals and finishing chemicals. Groundwater is used as the major source of water in Pakistan's leather industry.

The Environmental Challenge
Leather tanneries in Pakistan produce all three categories of waste: wastewater, solid waste and air emissions. However, wastewater is by far the most important environmental challenge being faced by Pakistan's tanneries.

Wastewater: Although the exact quantity varies widely between tanneries, a normal requirement of around 50-60 liters of water per kilogram of hide is suggested. ETPI's sample audits of tanneries in Pakistan show that in some cases the consumption of water is as high as three times the suggested requirement. The overall water discharge also demonstrates a high degree of seasonal and daily fluctuation. For most part, the current practice is to discharge this water into the local environment without any treatment.

Tannery wastewater is highly polluted and the contamination observed is many times beyond the limits set by the National Environmental Quality Standards (NEQS) for all important wastewater parameters (for details see Table 1).

<p>| Table 1: Pollution Levels in Tannery Effluents |</p>
<table>
<thead>
<tr>
<th>Parameters</th>
<th>*Raw sheep &amp; goat skins - 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>BOD5 (Unfiltered) 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 SO4 at 0 time settling</td>
<td>1814 - 3146</td>
<td>800 - 860</td>
<td>5480 - 6480</td>
<td>600</td>
</tr>
<tr>
<td>Sulphide 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 : 12,000 kg/day; Volume of wastewater : 600 m3/day
** Quantity of raw material : 5,500 kg/day; Volume of wastewater : 814 m3/day
*** Quantity of raw material : 10,000 kg/day; Volume of wastewater : 110 m3 /day

The high level of settleable matter is a major reason for the sludge in composite tannery wastewater. This sludge contains between 3.5-6.5% of solid content, 20-48% of volatile matter, and 51-74% of inorganic matter.

**Solid Waste:** Two types of solid wastes (tanned and untanned) are generated from leather production processes. Solid waste include dusted curing salts, raw trimmings, wet trimmings, dry trimmings, wet shavings, dry shavings, buffing, and packaging material. It is estimated that for a tannery averaging 10,000 kilograms of skins per day, a total of some 5,500 kilograms of solid waste would be produced per day. Table 2 presents a breakdown on this waste and its key characteristics.

### 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 Trimming</td>
<td>0.024 kg/skin</td>
<td>Proteins</td>
<td>The skins are trimmed (especially at legs, belley, neck, and tail parts) in order to give it a smooth shape. The trimmings are usually sold to soap and poultry feed makers.</td>
</tr>
<tr>
<td>Waste Type</td>
<td>Quantity/kg/skin</td>
<td>Composition</td>
<td>Uses</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------------</td>
<td>------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Fleshing</td>
<td>0.25</td>
<td>Contains around 240 gm/kg of proteins, 200 gm/kg of fats, 3 gm/kg of lime, 2 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</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 shavings from the tanners.</td>
</tr>
<tr>
<td>Dry Trimming/Dry Shaving/Buffing Dust</td>
<td>0.06</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 of the leather from the tanners.</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>

In general, it is found that solid wastes from tanneries (except for dusted salt) have secondary users in the local market. Glue manufacturing and poultry feed makers are a major user group of this waste. However, an important problem with this use is the presence of chromium in it. The use of chrome contained solid waste for poultry feed preparation could cause serious health problems for poultry consumers.

**Air Emissions**: There are two sources of air pollution from tanneries in Pakistan. The first relates to emissions from generators (diesel-based and operated only during power breakdowns) and from boilers. Emissions were found to be well below the NEQS level. Ammonia emission during processing and washing of drums, though intermittent but important, has adverse effects on workers health. Hydrogen sulphide emission during mixing of acid and alkaline wastewater in drain is also a serious health hazardous. Segregated discharge of acidic and alkaline effluent can help to avoid the hydrogen sulphide gas emission.

**Technologies of Change**
Various measures can be taken to address the environmental challenges faced by the leather sector in Pakistan. The most immediate of these are in-house measures related to waste reduction at source and adopting more environment friendly processes (see Box 1).

**Box 1: Towards Environment Friendly Tanneries**
Tanneries in Pakistan can take a number of steps to move towards more environment friendly production. A number of technological approaches exist which could also be a source of net economic saving for tanners. However, the applicability of these solutions varies from one tannery to the next depending on the nature of raw material, processing conditions, and type of finished product.

**Water Conservation:** Converting from continuous to sequential washing can lead to significant water saving and to a much reduced hydraulic load for the effluent treatment plant.

**Use of Environment Friendly Chemicals:** Enzymatic products can replace sulfides; surfactants, if used, should be biodegradable; use of Penta Chloro Phenol (PCP) should be avoided; weak organic acids can replace ammonium sulfate in deliming process; trivalent chromium should be used for tanning instead of hexavalent chromium which is toxic; metal complex dyes should be replaced; halogen containing hydrocarbons should be replaced by water finishers.

**Green Fleshing of Hides:** Green fleshing, just after deep soaking, results in pH close to neutral. This will result in savings on liming and unhairing chemicals and improve the penetration of chemicals into skins.

**Hair Savings Methods:** These require smaller quantities of sulfide and allow an easy separation of the protein constituted by the undissolved hair. This results in significant reductions in the COD, BOD5, Nitrogen, Sulfide, and Total Suspended Solids, thereby reducing the organic load for the treatment plant.

**Recycling Liming and Unhairing Liquors:** Improved liming and unhairing techniques permit a direct reuse of the spent liquors. This leads to savings in water, sulfide, and lime.

**Lime Splitting and Trimming:** Splitting and trimming is usually carried out after tanning by which time chromium has been introduced into the by-products. Savings in the amount of chemicals used for deliming, pickling, tanning, and consequently reduction in the pollutant load can be achieved if these procedures are carried out with the pelt. The non-tanned by-product will be good raw material for the manufacture of gelatine or animal feedstock.

**Oxidation of Sulfide:** Oxidizing the sulfide in the liquor through the use of hydrogen peroxide or sodium hydrogen sulfite will avoid the formation of hydrogen sulfide during the acidification of the deliming float.

**Finishing Process:** Conventional spray equipment wastes between 30-50% of the finish whereas a roll coating machine reduces the loss to about 5%. The conventional spray equipment should be equipped with proper scrubbing systems to reduce emissions.

A number of technologies exist to reduce and reuse the amount of chrome being lost to wastewater and sludge. About 25 - 30% of total of the chrome applied goes into the wastewater which can be reused. Amongst these options, three are of particular importance, the details of which are given in Box 2.

**Box 2: Chrome Reuse Options**

The **Direct Recycling of Chrome Tanning Float** is the easiest method to reuse the chromium in the process. After collecting and sufficiently fine screening, the float is recycled with the addition of fresh chromium. However, this technology has limitations related to quality and the need to control residual float. This solution is suitable for small tanneries.

The **Recycling of Chrome Through Precipitation** enables the recovery of tanning float, and the effluent from various post-tanning stages. After collection, screening and storage, the floats are precipitated with different types of alkalis and bases and the sludge is reused after simple settling and acidification. Large plants have operated under this scheme for many years in Germany, Italy, South America and France. Four such plants for chrome recovery have also been installed in Pakistan.

For the past few years **Tanning Products that Improve the Exhaustion Rate** have been available which enable a tanning cycle with very small quantities of chrome wastage. These products aim for the complete fixation of the chrome onto the protein fibers and leaving small quantity of unused chromium in the float.
End-of-pipe effluent treatment in tanneries at least requires two levels of treatment, primary and secondary. The primary treatment system includes mechanical screening, pH equalization and physiochemical processes. During this stage, coarse particulate flesh and hair is removed by means of perforated screens which also reduces the BOD load; the amplitude of pH fluctuation is reduced to a manageable and consistent range; and coagulation and flocculation are applied to remove suspended solids. During secondary treatment, biological processes are used to remove most of the organic matter from the wastewater by converting it into different gasses and into cell tissues. The most widely used processes for secondary treatment tend to be aerobic. However, anaerobic process is also utilized to some extent. The major technologies available for secondary treatment and their relative characteristics are presented in Table 3.

Table 3: Review of some important wastewater treatment technologies

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Technical Characteristics</th>
<th>Operational Characteristics</th>
</tr>
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</table>
| **Lagoons**  | Aerobic lagoons are deep earthen basins used for high strength organic wastewater with high solid concentration. Facultative lagoons are earthen basins filled with screened or primary effluent in which stabilization of waste is brought about by a combination of aerobic, anaerobic and facultative bacteria. Aerobic lagoons are large, shallow earthen basins used for treatment of wastewater by natural processes involving both algae and bacteria. Maturation ponds are low rate stabilization ponds usually designed to provide for secondary effluent polishing and seasonal nitrification. | • BOD5 loading kg/m$^3$/d – least efficient  
• BOD5 removal efficiency – 85 -90 %  
• Energy requirement for aeration kwh/kg BOD treated – moderately efficient  
• Hydraulic detention time—very high  
• mechanical complexity – low  
• Reactor resilience for power failure and shock loads – moderate to high  
• By-product – nil  
• On-site environmental impacts - soil infiltration and aerosoles dispersion  
• Land requirement --- large  
• Man power requirement – skilled  
• Frequency of repair & maintenance - medium |
| **Trickling Filters** | Wastewater flows from top to bottom, dispersed over filter material (stones, lava or plastic) during which soluble compounds are removed and, to a lesser extent, solids are taken up into the biofilm adhered to the carrier material. | • BOD5 loading kg/m$^3$/d – least efficient  
• BOD5 removal efficiency – 85 -90 %  
• Energy requirement for aeration kwh/kg BOD treated – most efficient (natural ventilation)  
• Hydraulic detention time—most |
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
</table>
| **Upflow Anaerobic Sludge Blanket (UASB) Reactor** | The basic idea of this system is that the flocs of anaerobic bacteria will tend to settle under gravity, when applying a moderate up-flow velocity of wastewater. In this way no separate sedimentation tank is necessary. The wastewater passes the reactor from bottom to top. To guarantee sufficient contact between the incoming wastewater and the bacteria in the sludge layer, the wastewater is fed evenly over the bottom of the reactor. Further mixing is brought about by the production of the gas. The organic compounds are consumed by anaerobic bacteria during passage of wastewater through sludge layer. | • BOD5 loading kg/m$^3$/d -- very efficient  
• BOD5 removal efficiency – 80 -90 %  
• Energy requirement for aeration kwh/kg BOD treated – most efficient (only for pumping)  
• Hydraulic detention time—most efficient  
• mechanical complexity – low  
• Reactor resilience for power failure and shock loads – moderate  
• By-product – bio-gas  
• On-site environmental impacts - nil  
• Land requirement --- small  
• Man power requirement – highly skilled  
• Frequency of repair & maintenance - low |
| **Activated Sludge Treatment**               | Many variations of activated sludge treatment exist, depending on load characteristics and local climatic conditions, the low loaded activated sludge system is efficient (recirculation is required)  
|                                            | • mechanical complexity – low  
• Reactor resilience for power failure and shock loads – moderate  
• By-product – nil  
• On-site environmental impacts - insects  
• Land requirement --- small  
• Man power requirement – skilled  
• Frequency of repair & maintenance - low |
the most relevant option. In this system, secondary sludge is digested in the same reactor. Wastewater to be treated is introduced into the reactor by mechanical stirring or by compressed air, where it is mixed with the mass of bacterial flocs maintained constantly in suspension. After sufficient contact time, the mixture is clarified in the settling tank and sludge is recycled in the aeration tank.

- BOD5 removal efficiency – 85 - 95 %
- Energy requirement for aeration kwh/kg BOD treated – least efficient
- Hydraulic detention time—moderately efficient
- mechanical complexity – high
- Reactor resilience for power failure – low and for shock loads – moderate
- By-product – nil
- On-site environmental impacts - aerosol dispersion and noise
- Land requirement --- moderate
- Man power requirement – highly skilled
- Frequency of repair & maintenance - very high

Lagoons, due to large land requirement, odour problem, possible groundwater contamination are not recommended. Trickling filter due to low efficiency and UASB system because of the complex characteristics of tannery wastewater and presence of sulphate are also not recommended. The low loaded activated sludge is a proven technology for treatment of tannery wastewater. Further local climatic condition - high temperature - also favours the digestion of the secondary sludge in the same reactor.

**Recommendations for Pakistan's Leather Sector**

Wastewater is the most critical environmental challenge facing Pakistan's leather sector. This is the priority area for environmental amelioration in this sector. This area requires major focus and calls for immediate attention and investment.

It is recommended that in-house improvements be undertaken immediately. This has the potential to reduce the pollutant as well as the hydraulic load to a level where end-of-pipe technologies may then be able to bring it down further to levels near, or below, the NEQS. Such measures are also likely to result in net savings for the tanneries in the long-term. A strategy for general remedial measures that can be immediately considered by all tanneries in Pakistan is presented in **Box 3**.

**Box 3: A General Strategy for Environmental Management in the Leather Sector**

| Short-term training on occupational health and safety, modern practices of handling chemicals, etc. should be conducted for tannery staff and operators. Information about safety, health and environment should be visibly displayed in the workspace. The provision and use of safety items such as face protective shields, acid resistant |
gloves, aprons, masks, etc. should be strictly enforced. Careful monitoring of water use needs to be implanted. Appropriate water conservation measures such as placing automatic stop valves on water supply pipes, converting from running water washing to batch washing, etc. should be adopted as appropriate. The appropriate environment friendly technologies listed in Box 1 should be adopted according to the particular needs and conditions of particular tanneries. Improvement in drainage system to avoid the formation of hydrogen sulfide gas inside the tanneries is suggested. Proper arrangements should be made to stop the use of tanned solid waste in the preparation of poultry feed. Chemical re-cycling should be practiced.

As far as end-of-pipe technologies are concerned, a combined treatment plant using low loaded activated sludge for secondary treatment is recommended as the preferred solution for Pakistan's tanneries. Box 4 highlights the key design and cost features of these recommended treatment systems. It should also be noted that the good housekeeping steps suggested in Box 3 would significantly reduce both the pollution and the hydraulic loads and can reduce the total cost of the treatment systems.

**Box 4: End-of-pipe Wastewater Treatment in Tanneries**

**Treatment of wastewater from tannery processing raw hides into finished leather.**
Design and cost estimation exercise was undertaken for a tannery where the complete process (from raw hides to finished leather) is undertaken. An average production load of 1,000 hides (approximately 12,000 kg/day) in normal operation and twice this load during the peak season was assumed. This translated to wastewater fluctuations ranging from around 1,800 m$^3$/day during normal operation to over 3,600 m$^3$/day during peak season. The respective pollution ranges were between 840 - 1,740 mg/l for BOD$^5$, 1,000-2,700 mg/l for COD, and 800 - 2,000 mg/l for total suspended solids.

Using a system similar to the one described above, NEQS compliance can be achieved. The cost of a treatment plant that is able to do is estimated at 45 million rupees, have an annual operating and maintenance cost of 15-20% of cost. The land requirement for the treatment plant and sludge drying beds is around 11,500-14,000 square meters.

**Treatment of wastewater from wet finishing processes.**
Design and cost estimates were undertaken for tanneries of two different sizes. The large tannery processing between 8,000-10,000 kg of wet blue skins per day. It was assumed that a medium sized tannery daily processed between 600-1,500 kg. This translates to water requirements of 80-120 m$^3$/day (averaged for the whole year) for the large tannery and 30-40 m$^3$/day for the medium sized tannery.

Based on the estimated daily pollution load a treatment system with the following specification is recommended:

Preliminary design suggests that such a system can bring down the pollution in wastewater from tanneries to a level allowed by NEQS. The system would require between 1,750-2,800 square meters of land for a large tannery (depending on whether mechanical dewatering is included or not) and between 160-210 square meters for a medium sized tannery. Cost calculations for the same (without the cost of land) suggests a total outlay of around ten million rupees for the treatment system in a large tannery and under three million rupees for a medium sized tannery. The estimated annual operation cost would be between 15-20% of the construction cost.
As already mentioned, the presence of chrome in wastewater from tanneries has serious environmental as well as economic consequences. It makes both economic and environmental sense to seek chrome recovery and reuse in Pakistan's leather sector. The economic feasibility of chrome recovery and reuse is discussed in Box 5.

**Box 5: The Economic Case for Chrome Recovery and Reuse**

As mentioned earlier, 25 - 30 % of the chrome that goes into the wastewater can be reused. The chrome tanning effluent from the tanning drum is the influent to the chrome recovery system. Addition of sufficient alkali to spent chrome liquor will cause precipitation of the chromium in the form of basic complexes. These are separated from the liquor by settling and/or filtering under pressure. The liquor is almost free of
chromium and contains most of the dissolved solids and other impurities. The chrome sludge cake can be dissolved in sulfuric acid to form a tanning liquor which can then be reused.

Preliminary estimates of the economic viability of chromium recovery and reuse in tanneries suggest that cost recovery can be achieved in 6 to 7 months for most tanneries. This assumes 95% chrome recovery, which is very much within the feasible range. The capital cost of such a plant for a tannery processing around 12,000 kg of hides per day is around one million rupees, while the cost is around 0.7 million rupees for a tannery processing 3,000 kg of hides per day.

FLOW DIAGRAM OF CHROME RECOVERY SYSTEM