Tannery Wastewater Treatment

- *Tanning means converting animal skin in to leather.*
- Oldest industry in India.
- This wastewater is characterized by strong colour, high BOD, high pH, high TDS.

- **Manufacturing process:**
- The tanning process consists of three basic stages:
  - Preparation of the hides for tanning,
  - Tanning proper,
  - Finishing.
Preparation of hides

• **Curing**: Involves dehydration of the hide by drying it with salt or air in order to stop proteolytic enzyme degradation.

• **Washing**: Removes the dirt, salts, blood, manure, and non-fibrous proteins.

• **Soaking**: It restores the moisture lost during preservation and storage by soaking in water containing sodium chloride and preservative chemical like “Antimucin” for 1 to 5 days. Soaked hides are washed again with sufficient water.
Preparation of hides

• **Unhairing:**
  - Hides are ‘limed’ with a paste of lime and with (or without) sodium sulfide.
  - Then hides are mechanically cleaned of hairs and fleshings.
  - This makes skin more attractive and more amenable to the removal of trace protein impurities.

• **Deliming and bating:**
  - Prepares the hides for tanning by reducing the pH, reducing the swelling and removing the protein degradation products in it.
  - Carried out in a vertical rotating drums in warm solutions of ammonium salts and commercially available proteolytic enzymes.
  - Bating makes leather slippery, smooth, increases width and diminishes its wrinkles.
Preparation of hides

• **Pickling:**
  – It is *required* for preparing the hide *for ‘chrome tanning’*. This involves the treatment of hides with sodium chloride and acid, to prevent precipitation of the chromium salts on the skin fibers.

• **Degreasing:**
  – Removes natural grease, thus *preventing formation of metallic soaps* and allows even penetration of tanning liquors.
II\textsuperscript{nd} Stage: Tanning Proper

- This makes hide non-putrescible and soft even when dried.
- Either \textit{vegetable substances} containing natural tannins such as extracts of barks, wood, nut, etc. are used or \textit{inorganic chromium salts} are used as tanning agents.
- Vegetable tanning is used for heavy leathers, while chromium tanning is used for the light leathers.
- In chrome tanning process the tanning is done in the same vat after one day of pickling by adding a solution of chromium sulphate.
- After four hours of tanning the leather is bleached with a dilute solution of sodium thiosulphate and \( \text{Na}_2\text{CO}_3 \) in same bath.
- A tanned leather is taken out, half of the spent liquor is thrown out and remaining is reused along with fresh volume of water.
- The vegetable tanned leathers are washed after the tanning proper.
IIIrd Stage: Finishing

- It consists of stuffing and fat-liquoring, followed by dyeing.
- **Stuffing and fat-liquoring** – the tanned leather is incorporated with oil and grease and thus becomes soft, pliable and resistant to tearing.
- **Dyeing** is done using synthetic dyestuffs.
Process flow chart

Continuous flow of wastewater

Raw hide

Soaking Pits

Liming Vats

Defleshing & Dehairing

Deliming

Tanning

Washing & finishing

Finished leather

Spent Soak Liquor

Soaking wash water

Liming wash water

Defleshing & Dehairing waste

Deliming wash water

Tanning wash water

Dyeing & Fat-liquoring wash water

Intermittent flow of wastewater

Spent Lime Liquor

Spent deliming and batting Liquor

Spent Tanning Liquor

Spent finishing Liquor
Sources of wastewater

- Wastewater originates from all the operations.
- It is either continuous from some operation or intermittent from few operations.
- Spent liquors from the soaking, liming, bating, pickling, tanning and finishing operation is discharged intermittently.
- Spent liquors are small in volume but highly polluted.
Sources of wastewater

• **Spent soak liquor:**
  
  - contains soluble proteins, dirt, common salt, etc.
  
  - It undergoes rapid putrefaction, nutrients are present for bacterial growth, even pathogens such as *anthrax* can grow.

• **Spent lime liquor:**
  
  - Contains dissolved and suspended lime, colloidal proteins, sulphides, fatty matter, un-reacted lime, calcium sulphide, CaCO$_3$, high alkalinity and moderate BOD.

• **Spent Bating liquor:**
  
  - Contains high amount of organic and ammonia nitrogen used in bating.
Sources of wastewater

- **Spent vegetable tan liquor:**
  - Contains tannins, high COD, low BOD and also non-tannins, e.g., salts, organic acids, sugar with high BOD and high COD
  - Strongest individual wastewater stream, dirty brown colour and acidic pH of 4.5 to 5.0.
  - When mixed with spent lime liquor this waste *yield bulky precipitate.*

- **Spent pickling and Chrome-tanning waste:**
  - Small volume, low BOD
  - Contains salts, mineral acids, chromium salts, protein impurities.
  - **Chromium** toxic in hexavalent form and less toxic in trivalent form.
  - When mixed with spent lime liquor most of the trivalent chromium is precipitated.
  - Segregation of spent chrome-tan liquor is advised for chemical recovery and better treatment. All other wastewaters are combined.

- **Spent dyeing & fat liquoring:** small in volume less significant.
## Average composition of spent liquors & combined wastes

<table>
<thead>
<tr>
<th>Item</th>
<th>Spent veg-tan liquor</th>
<th>Spent chrome tan-liquor</th>
<th>Combined waste</th>
<th>Spent soak liquor</th>
<th>Spent lime liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.4</td>
<td>3.2</td>
<td>8.9</td>
<td>8.4</td>
<td>12.8</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>-</td>
<td>-</td>
<td>260</td>
<td>600</td>
<td>1600</td>
</tr>
<tr>
<td>Acidity</td>
<td>2560</td>
<td>5400</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chloride</td>
<td>3000</td>
<td>-</td>
<td>4280</td>
<td>16800</td>
<td>8900</td>
</tr>
<tr>
<td>Total Solids, mg/L</td>
<td>34800</td>
<td>7480</td>
<td>10505*</td>
<td>35800</td>
<td>38240</td>
</tr>
<tr>
<td>SS, mg/L</td>
<td>2660</td>
<td>705</td>
<td>1080</td>
<td>4500</td>
<td>3590</td>
</tr>
<tr>
<td>COD</td>
<td>30240</td>
<td>3584</td>
<td>3700</td>
<td>3584</td>
<td>12000</td>
</tr>
<tr>
<td>BOD</td>
<td>16000</td>
<td>-</td>
<td>900 - 1725</td>
<td>708</td>
<td>7300</td>
</tr>
<tr>
<td>Chromium, mg/L</td>
<td>-</td>
<td>2800</td>
<td>- (30 – 70 mg/L from chrome tanning)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* - about 3000 mg/L NaCl
Effect of waste on receiving stream

- High BOD, high SS, strong colour,
- Rapid depletion of DO, due to chemical and biological oxidation of sulphur and organic compounds.
- Deposition of solids near discharge point.
- High chloride concentration results in water body (> 500 mg/L).
- Chromium is toxic to aquatic life, however, most of it gets precipitated when the waste is combined.
- Vegetable tannins are reddish tan in colour and become inky blue when come in contact with water.
- Application of wastewater on soil may make it unfertile.
- When discharged in sewers, chocking may occur due to deposition of solids. Lime encrustation due to CaSO$_4$ and CaCO$_3$ precipitation may occur. Release of H$_2$S may lead to corrosion of sewers.
- Chromium in excess of 10-20 mg/L disturbs biological treatment.
Environmental Standards

- Tannery effluent standard (after primary treatment) for discharge in channel/ conduit carrying wastewater to secondary treatment plant

<table>
<thead>
<tr>
<th>Type of Tanneries</th>
<th>Parameter</th>
<th>Concentration limit not exceed, mg/L (except pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome tanneries/ combined chrome &amp; vegetable tanneries</td>
<td>pH</td>
<td>6.5 to 9.0</td>
</tr>
<tr>
<td></td>
<td>SS</td>
<td>Not to exceed 600</td>
</tr>
<tr>
<td></td>
<td>Chromium, after treatment in chrome wastewater stream</td>
<td>45</td>
</tr>
<tr>
<td>Vegetable tanneries</td>
<td>pH</td>
<td>6.5 to 9.0</td>
</tr>
<tr>
<td></td>
<td>SS</td>
<td>Not to exceed 600</td>
</tr>
</tbody>
</table>
# Environmental Standards

## Tanneries: Effluent Standards

Wastewater generation : 28 m$^3$/tonne of raw hide processed

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration, mg/L, except pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5 to 9.0</td>
</tr>
<tr>
<td>BOD* (27°C, 3 days)</td>
<td>100</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>100</td>
</tr>
<tr>
<td>Sulphides (as S)</td>
<td>1</td>
</tr>
<tr>
<td>Total chromium (as Cr)</td>
<td>2</td>
</tr>
<tr>
<td>Oil &amp; grease</td>
<td>10</td>
</tr>
</tbody>
</table>

* - For effluent discharge into water body the BOD limit shall be made stricter to 30 mg/L by state pollution control board.
Treatment of Tannery waste

• Most of the tannery in India provide physical treatment only.

• **Screens**: Required to remove fleshing, hairs, and other floating matters. Screening can be used for glue manufacture or recover hair, fleshing & fats.

• **Sedimentation**: 4 hr HRT is effective in 90% removal of solids. It can be continuous flow or fill and draw type.
  
  – No appreciable reduction in TDS, COD, and BOD occurs in primary treatment. However, wastewater can be discharged in sewers after it.

• **Chemical coagulation** (with or without neutralization): Coagulant like alum, ferric chloride, ferrous sulphate can be used.
  
  – Ferrous sulphate is effective for colour, chromium, sulphide & SS removal from chrome-tan wastes.

  – Alum is used with prior neutralization by CO$_2$ or acid.
Biological treatment:

- Treatment in ASP when wastewater is mixed with sewage is feasible. About 90% removal of BOD and COD is possible.
- Chromium removal is necessary before biological treatment.
- Trickling filter can also be used.
- Anaerobic filter: 90% COD and 91 to 97% BOD removal can be obtained at HRT of 12 h.
- Low cost treatment such as oxidation pond, anaerobic lagoons followed by aerated lagoon can be used.

**Treatment of Tannery waste**

**Screening**

- Raw wastewater
- Screening

**PST**

- Sludge to drying beds
- Anaerobic Lagoon, DT = 10 d

**Aerated lagoon, DT = 6 d**

**Effluent**
Treatment of Tannery waste

• Normally residual chromium concentration after removal in PST will not have adverse effect on biological treatment.

• **NaCl removal** is a problem from this waste.
  – Spent soak liquor (10% NaCl) and pickling liquor (8% NaCl) can be segregated and treated separately by solar evaporation, when high NaCl results in the receiving streams.
  – Spent liquor reuse is more attractive.
  – Use of Neem oil or other preservatives than salt can also reduce the problem of NaCl.

• Segregation of spent chrome-tan liquor and **recovery of chromium** is often practiced.
  – Chemical precipitation of Chromium in the form of Cr(OH)$_3$ by lime at pH 6.6.
  – Separation of Cr(OH)$_3$ by sedimentation or filtration.
  – H$_2$SO$_4$ addition and recovery of chrome sulphate solution which can be reused.
  – Recovery can considerably reduce pollution.