TANNERY INDUSTRY

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.

- **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.

- **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.

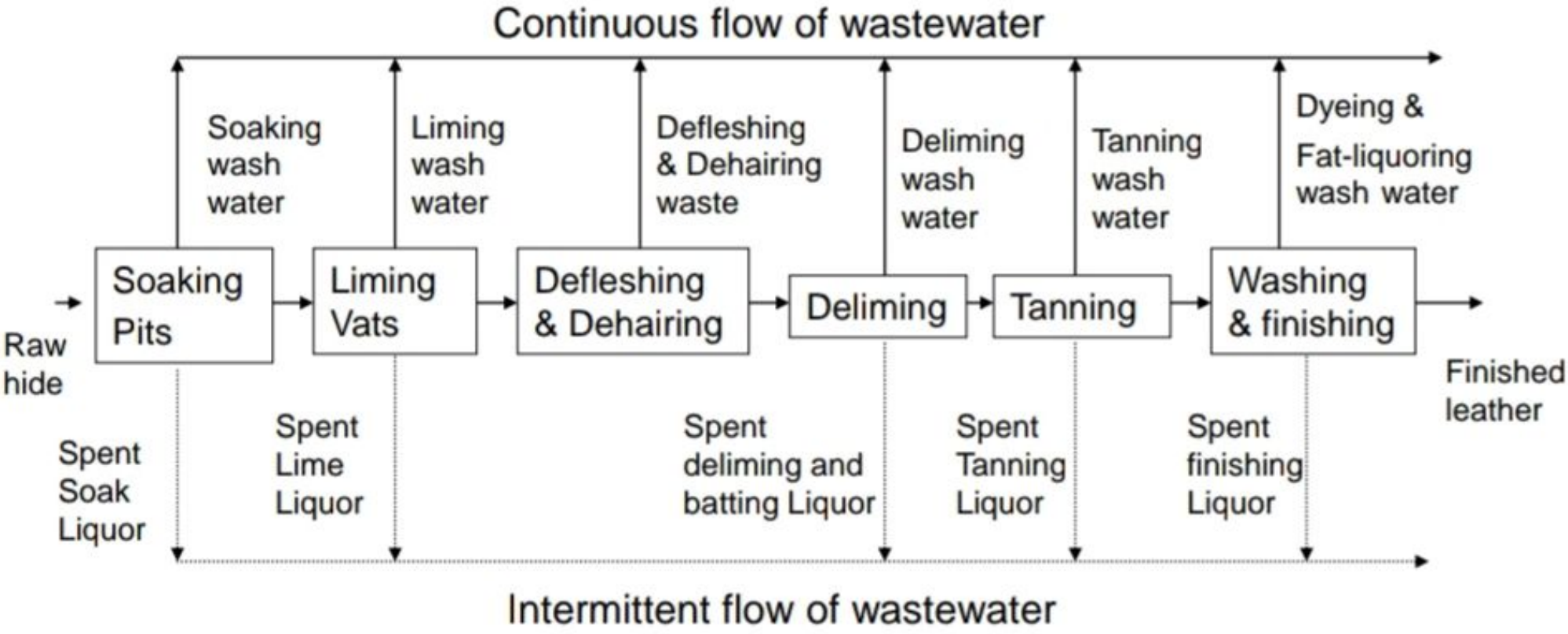
IInd Stage: Tanning Proper

- This **makes hide non-putrescible and soft even when dried**.
- Either ***vegetable substances*** containing natural tannins such as extracts of barks, wood, nut, etc. are used or ***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 Na_2CO_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



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.

- **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.

Effect of waste on receiving stream

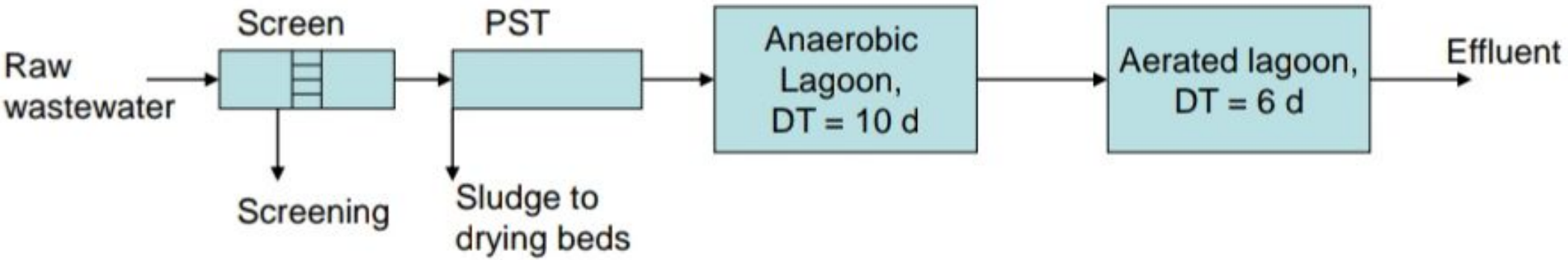
- High BOD, high SS, strong colour,
- Rapid depletion of DO, due to chemical and biological oxidation of sulphur and organic compounds.
- Deposition of solids near discharge point.
- High chloride concentration results in water body (> 500 mg/L).
- Chromium is toxic to aquatic life, however, most of 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_2S may lead to corrosion of sewers.
- Chromium in excess of 10-20 mg/L disturbs biological treatment.

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.



- 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.
- Segretation 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_2SO_4 addition and recovery of chrome sulphate solution which can be reused.
  - Recovery can considerably reduce pollution.

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