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.

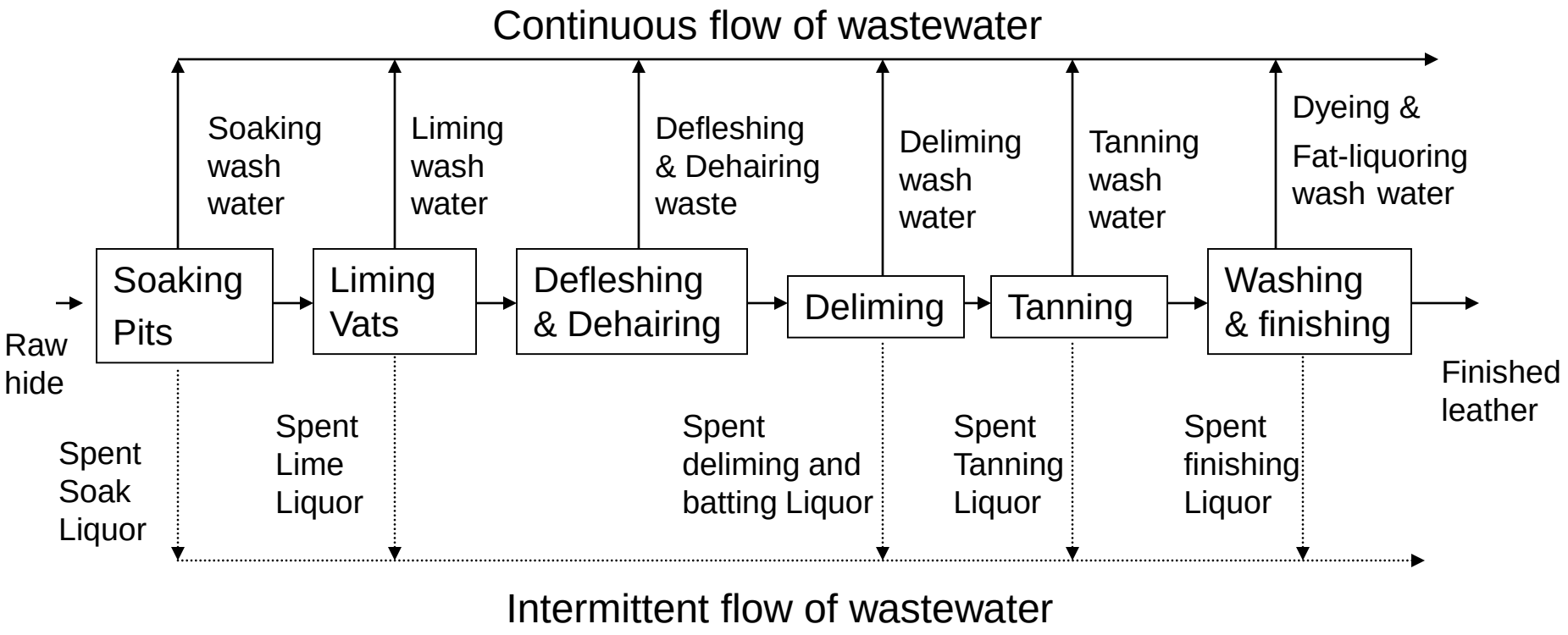
IInd Stage: Tanning Proper

- 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.

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

Item	Spent veg-tan liquor	Spent chrome tan-liquor	Combined waste	Spent soak liquor	Spent lime liquor
pH	5.4	3.2	8.9	8.4	12.8
Alkalinity	-	-	260	600	1600
Acidity	2560	5400	-	-	-
Chloride	3000	-	4280	16800	8900
Total Solids, mg/L	34800	7480	10505* (6000 – 8000)	35800	38240
SS, mg/L	2660	705	1080	4500	3590
COD	30240	3584	3700	3584	12000
BOD	16000	-	900 - 1725	708	7300
Chromium, mg/L	-	2800	- (30 – 70 mg/L from chrome tanning)	-	-

* - 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_2S 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

Type of Tanneries	Parameter	Concentration limit not exceed, mg/L (except pH)
Chrome tanneries/ combined chrome & vegetable tanneries	pH	6.5 to 9.0
	SS	Not to exceed 600
	Chromium, after treatment in chrome wastewater stream	45
Vegetable tanneries	pH	6.5 to 9.0
	SS	Not to exceed 600

Environmental Standards

Tanneries: Effluent Standards

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

Pollutant	Concentration, mg/L, except pH
pH	6.5 to 9.0
BOD* (27^{o}C, 3 days)	100
Suspended solids	100
Sulphides (as S)	1
Total chromium (as Cr)	2
Oil & grease	10

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

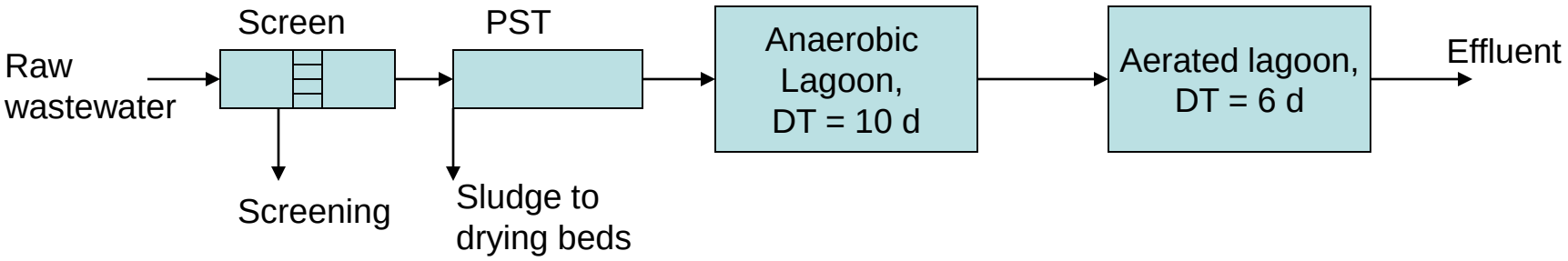
Treatment of Tannery waste

- 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.

Treatment of Tannery waste

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

- 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.