Pulp and Paper Mill
Environmental Standards

- LARGE PULP AND PAPER/NEWS PRINT/ RAYON GRADE PULP PLANTS OF CAPACITY 24000 TONNE/ANNUM: WASTEWATER DISCAHRGGE STANDARDS

<table>
<thead>
<tr>
<th>Parameter/ Flow</th>
<th>Concentration not to exceed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large pulp and paper</td>
<td>200 cum/ tonne of paper</td>
</tr>
<tr>
<td>Large rayon grade/news print</td>
<td>175 cum/ tonne of paper</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 to 8.5</td>
</tr>
<tr>
<td>SS</td>
<td>100 mg/l</td>
</tr>
<tr>
<td>BOD at 27°C for 3 days</td>
<td>30 mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>350 mg/l</td>
</tr>
<tr>
<td>TOCL*</td>
<td>2.0 kg tonne of paper produced</td>
</tr>
</tbody>
</table>

*The standards for total organic chlorine (TOCL) are applicable from January, 1992.

**TOCL** – Amount of organically bound chlorine that has carried over from the bleaching process into the wastewater. This specific test is carried out on samples of wastewater to determine TOCL content.
## Environmental Standards

**SMALL PULP AND PAPER INDUSTRY: STANDARDS FOR LIQUID EFFLUENTS**

<table>
<thead>
<tr>
<th>Mode of disposal</th>
<th>Parameter</th>
<th>Concentration not to exceed, mg/l (except for pH and SAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inland Surface Water</td>
<td>pH</td>
<td>5.5 to 9.0</td>
</tr>
<tr>
<td></td>
<td>Suspended solids</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>BOD at 27°C, 3 days</td>
<td>30</td>
</tr>
<tr>
<td>Land</td>
<td>pH</td>
<td>5.5 to 9.0</td>
</tr>
<tr>
<td></td>
<td>Suspended solids</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>BOD at 27°C, 3 days</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Sodium absorption ratio</td>
<td>26</td>
</tr>
</tbody>
</table>
Sodium adsorption ratio (SAR)

- It is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. It is also a measure of the sodicity of soil, as determined from analysis of water extracted from the soil.
- The formula for calculating sodium adsorption ratio is:
  \[
  \text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{1}{2}(\text{Ca}^{++} + \text{Mg}^{++})}}
  \]
  where sodium, calcium, and magnesium are in milli equivalents/liter.
- Although SAR is only one factor in determining the suitability of water for irrigation, in general, the higher the sodium adsorption ratio, the less suitable the water is for irrigation.
- If irrigation water with a high SAR is applied to a soil for years, the sodium in the water can displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure and tilth.
Environmental Standards

• Small pulp and Paper Industry: Wastewater Discharge Standards

• CATEGORY A: Agrobased
  – Before 1992 = 200 cum/tonne of paper produced
  – From 1992 = 150 cum/tonne of paper produced

• CATEGORY B: Waste Paper Based
  – Before 1992 = 75 cum/tonne of paper produced
  – From 1992 = 50 cum/tonne of paper produced
Pulp and Paper Mill Waste

• It is a materials industry.

• One of the major industries which contributes to water pollution.

• Few mills produce pulp alone and most of the mills produce paper and pulp.

• Pollution potential of paper mill is negligible compared to pulp mill.
Manufacturing Process and Sources of the Waste

- Manufacturing process two stage:
  - Pulp making
  - Paper production
Pulp Making

• When wood is received – bark is removed (either mechanically or hydraulically)
• Wood is reduced to chips for cooking.

• Mechanically prepared pulp (e.g. news paper)
  – Grinding of wood
  – carrying it by water through screens.
  – This produced coloured paper, low grade, non-durable.

• Chemically prepared pulps
  – Chipped cellulosic raw materials are digested with different chemicals under high temperature and pressure.
  – The process loosens cellulose fibers and dissolves the lignin, resin and other non–cellulosic materials in the raw material.
Pulp Making

• **Kraft Process** (or sulphate process)
  – Sodium sulphate, sodium hydroxide, sodium sulphide and carbonate (Na$_2$CO$_3$) are chemicals used for digestion.

• **Sulphite process**
  – Magnesium or calcium bisulphite and sulphurous acid are used.
  – Temperature 300 °F (150 °C) and 70 lb pressure, 5 to 6 hr.

• **Alkali Process**
  – Sodium hydroxide or lime is used (or mixture of Na$_2$CO$_3$ and Ca(OH)$_2$) for soft wood.
Pulp Making

• After digestion (by any of the process) the black liquor is allowed to drain from chemically prepared pulp.

• This spent liquor called as ‘black liquor’ is rich in lignin content and unutilized chemicals, therefore treated separately for chemicals recovery.

• ‘Black liquor’ from sulphite process is not treated for chemical recovery.

• The cellulosic fibers after separation from ‘black liquor’ are washed and then partially dewatered in a cylindrical screen called ‘Decker’.

• Concentrated wash water is sent for chemical recovery, dilute wash water forms wastewater.
Pulp Making

• Bleaching

  – Washed cellulosic fibers are bleached in three stages using **chlorine, caustic and hypochlorite** in successive stages.

  – Wastewater from **first and last stage is yellow in colour**, while from the **caustic extraction stage it is highly coloured**.

  – The dried, bleached pulp is ready for sale or use in paper mill.
Paper Mill

• Beater
  – The pulp is *disintegrated*, and mixed with *various filler materials* such as alum, talc etc. and dyes, in a special tank called as ‘beater’.
  – Beater is designed to *break up the knotted or bunched fibers* and cause a thorough mixing.
  – This is carried out with help of drum with knives attached to its wall and rotation.

• Jordan
  – After beating the pulp is *refined* in a machine known as ‘Jordan’.
  – This *cuts the fibers to the final size* desired. (with help of conical drums with knives)
Paper Mill

• Screens
  – The **pulp is then diluted** to proper consistency for paper making and **passed through the screen** to remove lumps or knots.

• Rolls
  – This pulp is carried by traveling belt of fine screen to series of ‘Rolls’ where the paper is produced.

  – The drain water called ‘**white water**’ forms the wastewater from the paper mill section. This contains fine fibers, alum and talc.

  – Usually fibers are recovered and rest liquid is reused for the wet chipping process.
Recovery of chemicals from black liquor

Black liquor → Evaporator → Furnace → Smelt → Green Liquor → Lime mud (contains lignin) → Burning → Lime (reused) → White Liquor

Water → Green Liquor

Lime reused in digestion
Recovery of chemicals from black liquor

• ‘Black liquor’ from kraft process
  – Concentrated by evaporation and incinerated.
  – The smelt is dissolved in water. This is called as ‘Green liquor’.
  – Lime is added to form ‘white liquor’ and lime mud
  – White liquor contains desired digestion chemicals and used in digestion.
  – Lime mud is calcined (by burning) to form Ca(OH)$_2$ which is reused in green liquor treatment.

• Small amount of wastewater is generated during wet chipping and bark removal.

• Some toxic waste material may develop during chemical recovery from black liquor e.g. Dimethyne Sulphide, Methyl Mercaptan and after condensation form colourless wastewater.
Semichemical pulping

- Use of hard wood for paper manufacturing is increased due to scarcity of soft wood.
- Semi-chemical pulping is used for this hard wood.
- Cooking under neutral pH with sodium sulphite
- Sometimes slightly acidic or basic pH values may be used.
- This softens the wood but does not fully pulp the wood.
- Pulping is carried out by mechanical means.
- Used for hard/coloured packing paper.
Production Process

Raw wood → Chipper house → Chips → Digester → Chemicals → Digester → Separation decker → Black liquor → Wash water → Chemical recovery → Water (White water is reused) → Wash water → Wash water (wastewater) → Wash water → Pulp → Washing → Washing
Production Process

Chlorine bleaching

Chlorination waste

Chlorine

Caustic bleaching

Caustic extraction waste (Coloured waste)

Caustic

Hypochlorite Bleaching

Hypochlorite waste

Light coloured waste (yellowish)

Finished pulp store

Glue, alum, talk

Beater
Production Process

Water

Knots

White water reused in chipping

Product
Characteristics of pulp and paper mill wastes

- Volume depends on manufacturing procedure and water economy adopted.
- Most of the Indian pulp mill operates on the Kraft process.
- Waste characteristics depend on size of plant, process used for pulping, and material recovery adopted.
- Chemical recovery is not practiced in small mills due to economic reasons.
- Wastewater is characterized as strong colour, high BOD, high SS high COD/BOD ratio.
## Characteristics of the combined effluent

<table>
<thead>
<tr>
<th>Item</th>
<th>Small mill, 20 tonnes paper per day</th>
<th>Large mill, 2000 tonnes of paper per day</th>
<th>Large mill with chemical recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>330 m$^3$/t</td>
<td>222 m$^3$/t</td>
<td></td>
</tr>
<tr>
<td>Colour</td>
<td>NA</td>
<td>7800 units</td>
<td>(100 -500)</td>
</tr>
<tr>
<td>pH</td>
<td>8.2 - 8.5</td>
<td>8.5 – 9.5</td>
<td>7.6 – 9.5</td>
</tr>
<tr>
<td>Total Solids, mg/l</td>
<td>NA</td>
<td>4410</td>
<td>800 – 2000</td>
</tr>
<tr>
<td>SS, mg/l</td>
<td>900 – 2000</td>
<td>3300</td>
<td>75 – 300</td>
</tr>
<tr>
<td>COD, mg/l</td>
<td>3400 – 5780</td>
<td>716</td>
<td></td>
</tr>
<tr>
<td>BOD, mg/l</td>
<td>680 – 1250</td>
<td>155</td>
<td>(100 – 350)</td>
</tr>
<tr>
<td>COD/BOD ratio</td>
<td>3.9 – 5.0</td>
<td>4 - 6</td>
<td></td>
</tr>
</tbody>
</table>

- Low values in large mills are due to chemical recovery from black liquor.
- Also, use of more quantity of water for washing of pulp.
The Effects on Receiving Water

- Pollution is extended to long stretch of river (> 80 km) due to presence of slow decomposing component (lignin).

- **Fine fibers** often clog the water intake screen.

- **Toxic effect** may be induced on aquatic life due to sulphites and phenols.

- Deposition of lignino–cellulosic material at discharge point undergo slow decomposition and may lead to DO depletion.

- Normally **not allowed to discharge in sewers** due to strong nature of waste.
Treatment of pulp and paper mill waste

- Pollution load can be reduced by lignin recovery from ‘black liquor’.
- Instead of incineration, where lignin is destroyed
  - Black liquor → precipitation of lignin
  - Acidification
    - CO₂ or H₂SO₄
- Separated lignin
  - Can be used as dispersing agent in various suspension
  - Raw material for polyacrylonitrile fibers
  - Production of activated carbon
- Fibers from ‘white water’ can be recovered by sedimentation or floatation.
Treatment of pulp and paper mill waste

• Chemical treatment for colour removal
  – Chemical coagulation for colour removal is **uneconomical**

• **Massive Lime Treatment**: 90% colour and 40-60% BOD removal
  – The quantity of lime required for green liquor is allowed to react with coloured waste effluent.
  – The colour is absorbed by the lime, sludge after settling is used for addition to ‘green liquor’ to form white liquor.
  – After treatment it will form dark brown liquor instead of white liquor.
  – This contain desired cooking chemicals and used in digester liquid.
  – The **coloured waste stream can be brown stock + caustic extraction waste and black liquor**, if no chemical recovery.
  – After digestion, the lignin present in the liquid will be destroyed along with ‘spent black liquor’ during incineration.
Treatment of pulp and paper mill waste

Caustic extraction waste → Lime
Brown stock wastewater

Lime → Lime Sludge

Green Liquor

Wastewater → Lime mud

Brown Liquor (used for digestion)

Lime mud → Burning

Ca(OH)₂
Treatment of pulp and paper mill waste

- **Activated carbon:** can remove 94% colour at pH 3.0

- **Clarification:**
  - 70 – 80 % of suspended solids can be removed from combined waste.
  - BOD reduction is small 25 – 40 %, COD removal 50%.
  - Sludge can be dewatered mechanically.

- **Biological Treatment:**
  - Both conventional and low cost treatment methods can be used
  - Some are even effective in colour removal.
Treatment of pulp and paper mill waste

- **Waste stabilization pond**: 0.9 – 1.5 m depth, DT = 12 to 30 days, 85% BOD removal.

- **Aerated lagoon**: DT = 3 to 20 days up to 95% BOD reduction. At loading 670 to 1340 kg BOD / hectare. Day.

- Nitrogen and phosphorous addition may be necessary for biological treatment.

- **Anaerobic lagoon**: DT = 6 – 20 days, 0.05 to 0.02 kg BOD/m$^3$.d; 70 to 77 % BOD removal

- **Activated sludge process**:
  - Most effective, surface aerator works better than diffuser due to problem of clogging.
  - 80 to 90% BOD removal (F/M = 0.2 to 0.3); DT = 3 – 9 hr. N & P addition is necessary.

- Trickling filter has limited use due to clogging of filter bed by fibers.
Treatment of pulp and paper mill waste

Black Liquor

- Lime Treatment
  - Flow = 4%
  - BOD = 80%

- Clarifier
- Cooling Tower
  - BOD rem = 90%
  - DT = 25 days

- Anaerobic lagoon
  - BOD rem = 80%
  - DT = 15 days

Other waste
- Grit Chamber
- Clarifier
  - Calcium Hypochlorite
    - BOD rem = 40-50%
    - Colour rem = 70%
    - DT = 15 days

- Stabilization Tank
- Aerated lagoon
  - DT = 3 days