Chapter 2

REVIEW OF LITERATURE

2.1. Paper Industry

The manufacturing of pulp and paper has negative impact on environment. The manufacturing process that transforms wood from trees into thin uniform paper products requires the intensive use of water energy and chemicals. This process also consumes thousands of gallons of a finite resource, clean water, to make each ton of paper. Pollution literally represents a waste of these resources, in the form of air emissions, waterborne wastes (effluent), solid waste and waste heat. Among primary manufacturing industries, paper manufacturing is the fourth-largest user of energy and the largest generator of wastes, measured by weight (NREL, 1995). In this resource-intensive industry, environmental issues will always be an intrinsic part of manufacturing, especially since awareness of these impacts has increased among communities near mills and customers alike. History of paper mill shows that the first writing materials were Egyptian and Chinese silk cloths and the fibrous cellulose material containing plant material and China grass (*Boehmeria nivea*) was first used in China to manufacture paper (Carruthers, 1947). By the year 1150 the technology of paper making was entering into the Europe market through Moorish Spain. The raw material for paper making from the year 1150 to the middle of the 19th century was recycle cellulosic material such as rags, rope, fish nets and burlap. The flax pant was used for the production of special paper that is soft and strong. Today, most of the world’s bank notes are printed upon a high-value flax paper. Globally paper industry was distributed all over the worlds. But, in our study we are discussing about pulp and paper industry located in India. The paper industry holds a considerable share among the manufacturing sectors. Paper mills in India can be categorized into three groups based on the raw materials used by the industry. These are wood/forest based mills, agro-residue based mills and waste paper based mills. Availability of wood based raw materials on a sustained basis is a challenge and therefore mills rely on their captive plantation and from the farm forestry by growing trees in the periphery of the
agricultural fields. Due to the problems in availability of wood based raw materials, the share of non-wood based raw materials and recycled fibers has increased significantly. In 2006, around 70% of the total paper production was from non-wood raw materials and the recycled fibers and rest 30% comes from wood based raw materials (IPMA, 2006).

Today, 715 small and big paper mills produce a variety of different paper, paperboard as well as newsprint products in India with an installed capacity of around 10 million tonnes (Selvarthi and Ramasubramanian, 2010). India is the 15th largest paper producer in the world. The consumption of paper and paperboard in India was 9.18 million tonnes in 2009-2010. The growth in production of paper from less than 0.15 million tonnes in 1950 to 8.6 million tonnes in 2009-2010 is remarkable. During this period, the number of paper mills has increased from just 17 units in 1951 to 715 units. Out of 715 paper mills operating in India, 165 are based on agro-based raw materials and 30 on bamboo and wood (Thapliyal et al., 2009). About 194 paper mills, particularly small mills, are closed due to various reasons like environmental noncompliance. The per capita consumption of paper in India is very low i.e. 8.3 kg in 2008, as compared to an average consumption of 28 kg and 58 kg in Asia and world respectively (Saini, 2011). According to Xavier and Stella (2010), per capita consumption in China is 42 kg and 350 kg in developed countries. The per capita consumption is expected to increase to 12 kg by 2020. According to ITC’s estimates, the total demand for paper is around 8.0 million tonnes and is expected to grow to 10.0 million tonnes by 2012 and 21.0 million tonnes by 2020 (www.slideshare.net/indian-paper-industry-presentation-United States).

2.2. Pulp and Paper Manufacturing

2.2.1. Raw Materials

The papermaking process requires four major inputs: a source of fibre, chemicals, energy and water.

2.2.1.1. Source of Fibre

Wood is a primary source of fibre and composite material consisting of flexible cellulose fibres. The three main component groups of wood are cellulose,
hemicellulose, and lignin. Although the concentration of these three components can vary from species to species, the proportions are roughly 50% cellulose, 25% hemicellulose and 25% lignin.

(i) Cellulose

Cellulose is a very long linear molecule composed of repeating glucose units. Bundles of cellulose molecules from micro fibrils, build up to fibrils, and finally to cellulose fibers. Hydrogen bonding takes place between linear molecules to result in a strong microcrystalline structure. Cellulose is a polysaccharide with 600 to 1,500 repeated sugar units. The fibres have high tensile strength and absorb the additives used to modify pulp into paper and board products, and are supple, chemically stable and white.

(ii) Hemicellulose

Hemicellulose is composed of a random arrangement of five-carbon sugars. These long-branching molecules surround the cellulose fibers, and intrude into pores in the cellulose. Hemicellulose forms chemical bonds with the next layer lignin, and essentially acts as a chemical bonding agent between cellulose and lignin.
(iii) Lignin

Lignin is a complex phenyl propanoid polymer that surrounds and gives strength to the cellulose-hemicellulose framework. Lignin is composed of three phenol-based building blocks that polymerize in a completely random fashion. This random structure is very difficult to degrade. When slow degradation does take place, phenolic compounds, which are generally toxic, are released. The aromatic content of lignin, expressed as monomeric phenol, is approximately 51%. It is the phenolic compounds released from lignin during the chlorine bleaching of pulp that are responsible for a large percentage of the toxic compounds released in pulp mill effluents.

![Lignin](image)

(iv) Extractives

In addition, wood contains 1.5 – 5% extractives, a general designation for wood components that may be extracted by organic solvents. These include resin acids, fats, waxes, terpenoid compounds, tannins, flavonoids and troppolines. While extractives are generally present in mill wastes at much lower concentrations than phenolic materials, some of these compounds are relatively toxic, and can significantly reduce water quality and marine habitat in the lakes and rivers that receive mill effluents. The relative proportions of these components vary according to the fibre source as shown in table 2.1.
Table 2.1: Chemical constituents of pulp and paper fiber source (%)

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Softwood</th>
<th>Hardwood</th>
<th>Straw</th>
<th>Bamboo</th>
<th>Cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>38-46</td>
<td>38-49</td>
<td>28-42</td>
<td>26-43</td>
<td>80-85</td>
</tr>
<tr>
<td>Hemi-cellulose</td>
<td>23-31</td>
<td>20-40</td>
<td>23-38</td>
<td>15-26</td>
<td>Nd</td>
</tr>
<tr>
<td>Lignin</td>
<td>22-34</td>
<td>16-30</td>
<td>12-21</td>
<td>20-32</td>
<td>Nd</td>
</tr>
<tr>
<td>Extractive</td>
<td>1-5</td>
<td>2-8</td>
<td>1-2</td>
<td>0.2-5</td>
<td>Nd</td>
</tr>
<tr>
<td>Minerals and other inorganics</td>
<td>0.1-7</td>
<td>0.1-11</td>
<td>3-20</td>
<td>1-10</td>
<td>0.8-2</td>
</tr>
</tbody>
</table>

Note: Nd = no data available.

Wood is the primary source of fiber but some secondary sources include straws from wheat, rye and rice; canes, such as bagasse; woody stalks from bamboo, flax and hemp; and seed, leaf or bast fibers, such as cotton, abaca and sisal are also used for pulp and paper manufacturing. The majority of pulp is made from virgin fiber, but recycled paper accounts for an increased proportion of production. Paper recycling professionals recognize numerous grades and sub-grades of recovered paper, such as old newspapers, old corrugated containers and sorted office paper.

2.2.1.2. Chemicals

Manufacturing pulp and paper from wood is a chemical-intensive process. In kraft and sulphite pulping (described in section 2.2.2.2 below), the cook wood chips are dipped in a chemical solution to dissolve the lignin that binds the fibres together. Caustic soda (NaOH) solution was used for processing of recovered fibres. Mills also use combinations of chlorine and oxygen based chemicals to bleach or brighten the pulp. Numerous coatings, fillers and other additives are added to the pulp during the paper making process to facilitate manufacturing and meet the functional requirements of different types of paper.

2.2.1.3. Energy

Pulp and paper mills use a combination of electricity and steam throughout the papermaking process. Mills consume about 31 million british thermal unit (BTU) of energy to produce a ton of paper or paperboard. The source of this energy depends on
the type of pulping process up to certain level. Chemical pulping processes have special recovery systems that allow them to convert wood waste from the pulping process into electricity and steam. Mechanical pulping processes (described below) that convert more of the wood into pulp have less wood waste to burn, and therefore must purchase electricity or fossil fuels to meet their energy needs.

2.2.1.4. Water

Water is the basic process medium of pulp and paper manufacturing; it carries the fibres through each manufacturing step and chemical treatment, and separates spent pulping chemicals and the complex mixture of organic residues from the pulp. Papermaking processes use significant amounts of water. Average water use ranges from about 150-200m$^3$ per ton of product depending on the processes used and the products made at the mill.

2.2.2. Manufacturing Process

The pulp and paper manufacturing process can be divided into four steps: wood handling and debarking, pulping, bleaching and paper making.

2.2.2.1. Wood Handling and Debarking

Wood may arrive at a pulp mill wood yard in the form of raw logs or as chips from a lumber mill. Wood is converted into chips suitable for pulping in a series of steps which may include debarking, sawing, chipping and screening. Logs are debarked because bark contains little fibre, which contains high content of extractives; it is dark in colour, and often carries large quantities of grit. Debarking can be done hydraulically with high-pressure water jets, or mechanically by rubbing logs against each other or with metal cutting tools. Hydraulic debarkers may be used in coastal areas; however, the effluent generated contributes to water pollution. Chippers tend to produce chips with a considerable size range, but pulping requires chips of very specific dimensions to ensure constant flow through refiners and uniform cooking in digesters. Chips are therefore passed over a series of screens whose function is to separate chips on the basis of length or thickness. Oversized chips are re-chipped, while undersized chips are either
used as waste fuel or are metered back into the chip flow. The chips are then discharged from the stack base with help of screws and conveyors and sent to the pulping process (Ljungberg and Brannvall, 2011) (figure 2.1).

![Process of wood handling and debarking](image)

**Figure 2.1:** Process of wood handling and debarking

### 2.2.2.2. Pulping

Pulping is the process by which the bonds within the wood structure are ruptured and soften either mechanically or chemically. (Pokhrel and Viraraghavan, 2004) (figure 2.2).

![Process of pulping](image)

**Figure 2.2:** Process of pulping
(i) Chemical Pulping

In chemical pulping, fibres are released from the wood matrix with use of chemicals in the presence of heat and pressure. The reaction continues to a certain predefined degree of delignification and the products receive a good strength. The fibre yield for chemical pulping is often around 40-50%, and the rest is burned in the recovery boiler or considered as by-product (Hultman, 1997). The Kraft process is the dominating chemical pulping technology worldwide (FAOSTAT, 2012). The process is based on an alkaline solution of sodium hydroxide (NaOH) and sodium sulphide (Na$_2$S), which degrades the carbohydrates (hemicelluloses and lignin) by alkaline and peeling hydrolysis. Another common method is the sulphite process, which is a very popular process, based on an acidic or neutral cooking with salts of sulphites (SO$_3^{2-}$) or bisulphates (HSO$_4^-$) and bases like calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), ammonium (NH$_4^+$) or sodium (Na$^+$) etc. (Hultman, 1997).

(ii) Mechanical Pulping

In mechanical pulping, wood is processed mechanically with use of electrical energy. By utilizing a mechanical approach for fibre disintegration, the original composition of the wood is retained within the derived fibres, resulting in a high yield of the process (up to 95%) (Pokhrel and Viraraghavan, 2004). The manufacturing process is simpler than for chemical pulping, partly because there is no need for chemical recovery systems. However, the quality of the pulp is low grade and contains a lot of lignin which can cause post yellowing if applied to papers (Hultman, 1997). There are two main types of mechanical pulp; ground wood pulp and refined pulp. In the manufacturing of ground wood pulp, debarked logs are pressed against a rotating cylinder constructed of sheets with ceramic sandstone. The refined pulp is produced by grinding the wood chips between disc refiners, and fibres are released as chips are heated and beaten between the disc(s). There are several types of refined pulp, but Thermo-Mechanical pulp (TMP) and Chemo-Thermo-Mechanical pulp (CTMP) are the most common ones. If the chips are partially softened with steam before entering the
disc refiners, the produced pulp is referred to as TMP. If chemicals are added in addition to the heat, CTMP is produced (Hultman, 1997).

(iii) Bleaching

Bleaching is a multi-stage process to give the paper a specific brightness in order to obtain a certain printing quality and to purify the pulp from undesirable impurities that may be present in the final paper quality (Ljungberg and Brannvall, 2011). The objective is to dissolve (chemical pulps) or modify (mechanical pulps) the brown-coloured lignin that was not removed during pulping, while maintaining the integrity of the pulp fibres (figure 2.3).

![Figure 2.3: Process of bleaching](image)

Each bleaching stage is defined by its bleaching agent, pH, temperature and duration (Table 2.2). After each bleaching stage, the pulp may be washed with caustic to remove spent bleaching chemicals and dissolved lignin before it progresses to the next stage. After the last stage, the pulp is pumped through a series of screens and cleaners to remove any contaminants such as dirt or plastics. It is then concentrated and conveyed to storage. The process often starts with oxygen delignification where residual lignin is removed. The brightness can however only be increased marginally, which is why further bleaching steps are required.
Table 2.2: Bleaching agents and their conditions of use

<table>
<thead>
<tr>
<th>Bleaching agents</th>
<th>Symbol</th>
<th>Concentration of agent (%)</th>
<th>pH</th>
<th>Consistency (%)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine (Cl$_2$)</td>
<td>C</td>
<td>2.5–8</td>
<td>2</td>
<td>3</td>
<td>20–60</td>
<td>0.5–1.5</td>
</tr>
<tr>
<td>Sodium hydroxide (NaOH)</td>
<td>E</td>
<td>1.5–4.2</td>
<td>11</td>
<td>10–12</td>
<td>&lt;80</td>
<td>1–2</td>
</tr>
<tr>
<td>Chlorine dioxide (ClO$_2$)</td>
<td>D</td>
<td>≥1</td>
<td>0–6</td>
<td>10–12</td>
<td>60–75</td>
<td>2–5</td>
</tr>
<tr>
<td>Sodium hypochlorite (NaOCl)</td>
<td>H</td>
<td>1–2</td>
<td>9–11</td>
<td>10–12</td>
<td>30–50</td>
<td>0.5–3</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>O</td>
<td>1.2–1.9</td>
<td>7–8</td>
<td>25–33</td>
<td>90–130</td>
<td>0.3–1</td>
</tr>
<tr>
<td>Hydrogen peroxide (H$_2$O$_2$)</td>
<td>P</td>
<td>0.25</td>
<td>10</td>
<td>12</td>
<td>35–80</td>
<td>4</td>
</tr>
<tr>
<td>Ozone (O$_3$)</td>
<td>Z</td>
<td>0.5–3.5</td>
<td>2–3</td>
<td>35–55</td>
<td>20–40</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Acid washing (SO$_2$)</td>
<td>A</td>
<td>4–6</td>
<td>1.8–5</td>
<td>1.5</td>
<td>30–50</td>
<td>0.25</td>
</tr>
<tr>
<td>Sodium dithionite (NaS$_2$O$_4$)</td>
<td>Y</td>
<td>1–2</td>
<td>5.5–8</td>
<td>4–8</td>
<td>60–65</td>
<td>1–2</td>
</tr>
</tbody>
</table>

Historically, the most common bleaching sequence used to produce market-grade bleached kraft pulp is based on the five-stage CEDED process. The first two stages of bleaching complete the delignification process and are considered extensions of pulping. Because of environmental concerns about chlorinated organic in pulp mill effluents, many mills substitute chlorine dioxide (ClO$_2$) for a portion of the chlorine (Cl$_2$) used in the first bleaching stage (C$_0$EDED) and use oxygen (O$_2$) pre-treatment during the first caustic extraction (C$_0$D$_0$EDED). The current trend is towards complete substitution with ClO$_2$ (DEDED) or elimination of both Cl$_2$ and ClO$_2$. Where ClO$_2$ is used, sulphur dioxide (SO$_2$) is added during the final washing stage as an “antichlor” to stop the ClO$_2$ reaction and to control the pH. Newly developed chlorine-free bleaching sequences (AZQP, OQPZP, where Q = chelation) use enzymes, oxygen (O$_2$), ozone (O$_3$), hydrogen peroxide (H$_2$O$_2$), peracids and chelating agents such as ethylene diamine tetracetic acid (EDTA). Sulphite pulps are generally easier to bleach than Kraft pulps because of their lower lignin content. Short bleaching sequences (CEH, DCEHD, P, HP, EPOP) can be used for most paper grades.
2.2.2.3. Paper Manufacturing

A paper mill can either be integrated with the pulp mill or non-integrated. In the latter case, pulp is bought and transported to the paper mill. The end product of pulp and paper mills depends on the pulping process, and may include market pulp and various types of paper or paperboard products. Although similar in principle but the process of paper making is more complex than making pulp sheets. Some mills use a variety of different pulps to optimize paper quality (e.g., weak mechanical pulp, kraft pulp, sulphite pulp, chemi-mechanical pulp and recycled pulp) (figure 2.4).

![Figure 2.4: Process of papermaking](image)

The weak mechanical pulp is converted into single-use products such as newspapers and tissue. Kraft pulp is converted into multi-use paper products such as high-quality writing paper, books and grocery bags. Sulphite pulp, which is primarily cellulose, can be used in a series of diverse end-products including specialty paper, rayon, photographic film, TNT, plastics, adhesives, and even ice-cream and cake mixes. Chemi-mechanical pulps are exceptionally stiff, ideal for the structural support needed for corrugated container board. The fibres in pulp from recycled paper are usually shorter, less flexible and less water permeable, and can therefore not be used for high-quality paper products. Recycled pulp is therefore mainly used for the production of soft paper products like tissue paper, toilet paper, paper towelling and napkins.

Depending on the type of pulp used, a series of steps is necessary prior to forming the paper sheet. Generally, dried market pulp is rehydrated, while high-consistency pulp from storage is diluted. Pulp fibres may be beaten to increase the fibre-bonding area and thereby improve paper sheet strength. The pulp is then blended with “wet-end” additives. Wet end additives are used to improve the tensile properties of the paper both in wet and dry state by cross-linking the cellulose fibers with covalent bonds that do not break upon wetting (Table 2.3).
Table 2.3: List of wet additives used in paper manufacturing

<table>
<thead>
<tr>
<th>Additive</th>
<th>Location applied</th>
<th>Purpose and/or examples of specific agents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Most commonly used additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talc</td>
<td>Wet end</td>
<td>Pitch control (prevent deposition and accumulation of pitch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filler (make brighter, smoother, more opaque)</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Wet end</td>
<td>Pigment (brighten sheet, improve printing)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filler (make brighter, smoother, more opaque)</td>
</tr>
<tr>
<td>&quot;Alum&quot;(Al₂(SO₄)₃)</td>
<td>Wet end</td>
<td>Precipitates rosin sizing onto fibres</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Retention aid (fix additives to fibres, improve pulp fibre retention)</td>
</tr>
<tr>
<td>Rosin</td>
<td>Wet end</td>
<td>Internal sizing (resist liquid penetration)</td>
</tr>
<tr>
<td>Clay (kaolin)</td>
<td>Wet/dry</td>
<td>Filler (make brighter, smoother, more opaque)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pigment or surface coating (impart colour)</td>
</tr>
<tr>
<td>Starch</td>
<td>Wet/dry</td>
<td>Surface sizing (resist liquid penetration)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry strength additive (increase strength, reduce surface lint)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Retention aid (bind additives to paper, improve pulp fibre retention)</td>
</tr>
<tr>
<td>Dyes and pigments</td>
<td>Wet/dry</td>
<td>Acid, base or direct dyes, colour lakes, CaCO₃, may also include solvent vehicles</td>
</tr>
<tr>
<td>Latex</td>
<td>Dry end</td>
<td>Adhesive (reinforce sheet, bind additives to paper, fill pores)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waterproofing (resist liquid penetration)</td>
</tr>
<tr>
<td><strong>Other additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slimicides</td>
<td>Wet end</td>
<td>Thiones, thiazoles, thiocyanates, hiocarbamates, thiols, isothiazolinones, formaldehyde, glutaraldehyde, glycols, naphthol, chlorinated and brominated organics, organic mercury compounds</td>
</tr>
<tr>
<td>Defoamers</td>
<td>Wet end</td>
<td>Pine oil, fuel oil, recycled oils, silicones, alcohols</td>
</tr>
<tr>
<td>Wire treatment agents</td>
<td>Wet end</td>
<td>Imidazoles, butyl diglycol, acetone, turpentine, phosphoric acid</td>
</tr>
<tr>
<td>Wet and dry strength additives</td>
<td>Wet end</td>
<td>Formaldehyde resins, epichlorohydrin, glyoxal, gums, polyamines, phenolics, polyacrylamides, polyamids, cellulose derivatives</td>
</tr>
<tr>
<td>Coatings, adhesives and plasticizers</td>
<td>Dry end</td>
<td>Aluminium hydroxide, polyvinyl acetate, acrylics, linseed oil, gums, protein glues, wax emulsions, azite, glyoxal, stearates, solvents, polyethylene, cellulose derivatives, foil, rubber derivatives, polyamines, polyesters, butadiene-styrene polymers</td>
</tr>
<tr>
<td>Others</td>
<td>Wet/dry</td>
<td>Corrosion inhibitors, dispersants, flameproofing, antitarnish agents, drainage aids, deflocculants, pH control agents, preservatives</td>
</tr>
</tbody>
</table>

After that the blended pulp is passed through a final set of screens and cleaners. To produce market pulp, the pulp slurry is usually screened once more and its consistency is adjusted (4 - 10%) before it is ready for the pulp machine. The pulp is then spread
onto a travelling metal screen or plastic mesh (known as the “wire”). The excess water from the speeded pulp was drained out, leaving behind the web of fibres. The pulp sheet is passed through a series of rotating rolls (“presses”) that squeeze out water and air until the fibre consistency is 40 - 45%. The sheet is then floated through a multi-storey sequence of hot-air dryers until the consistency is 90-95%. Finally, the continuous pulp sheet is cut into pieces and stacked into bales. The pulp bales are compressed, wrapped and packaged into bundles for storage and transport (Ljungberg and Brannvall, 2011).

2.3. Waste Water Treatment

The papermaking industry is one of the biggest users of water and generates large quantities of highly polluted wastewater. Wastewater is released from every unit i.e., wood handling and debarking, pulping, bleaching and paper manufacturing which collectively discharged in to environment. Great pressure from environmental authorities, local regulations, consumers, and economic issues has forced the papermaking industry to apply technologies for wastewater minimization and proper wastewater treatment. Water recycle/reuse (closing the loops) is the most common technique used for fresh water and wastewater reduction in paper industry. However, water system closure without appropriate treatment is associated with an increase in organic and inorganic contaminant concentration in mill process water streams. It may have a negative impact on product quality, and could result in accelerated scaling and corrosion problems of papermaking equipment, odors in water and paper, deposits of sticky material, increase in biological activity in the mill process water (slime growth), and influence on efficiency of paper making chemicals (Malmqvist et al., 1999; Berard, 2000).

There is a large variety in external treatment technologies used for pulp and paper mill effluents and the preferred technology depends on many factors; characteristics of the matter to be removed, requirements on the purity of the effluent water, economical factors etc. Waste water treatment can involve primary (physical), secondary (biological) or tertiary (chemical) processes or combinations of these processes (figure 2.5). Primary treatment is mainly based on a physical removal of solids, secondary treatment on removal of dissolved organic compounds, and tertiary treatment used for
effluent polishing and elimination of more constituents. The use of tertiary treatments is rare at present, but can be an obligation in future due to possible new legislation (Thompson et al., 2001).

![Diagram of wastewater treatment stages]

**Figure 2.5**: Stages in wastewater treatment

### 2.3.1. Primary Treatment

The aim of primary treatment is to reduce suspended solids such as fibres, fibre debris, bark particles, filler and coating materials of effluent by use of screens, and settling tanks. Primary treatment devices are therefore designed to: (i) remove or to reduce in size the large, entrained, suspended or floating solids. These solids consist of pieces of wood, cloth, paper, plastics, garbage, etc. (ii) Remove heavy inorganic solids such as sand and gravel as well as metal or glass. These objects are called grit (iii) Remove excessive amount of oil or grease.

Primary treatment of effluents consists of two main processes, preliminary treatment and primary sedimentation. Primary treatment devices reduce the velocity and dispense the flow of waste water. In primary treatment, the velocity of flow is reduced to 1-2 feet per minute to maintain a quiescent condition so that the material denser than water will settle out and material less dense than water will float to the surface.

### 2.3.1.1. Preliminary Treatment

Pre-treatment, which includes screening and grit removal, is carried out at the start of the treatment process. Pre-treatment is designed to remove solid objects, along with
grease and oil, which impede efficient wastewater treatment and are undesirable in the end product bio-solids (Ochre-Media, 2001). Removal of solid objects is also undertaken to protect machinery (especially pumping equipment) and to prevent blockages in smaller pipes and channels, which transport the wastewater around the treatment plant. Pre-treatment also reduces the biochemical oxygen demand (BOD) of the wastewater.

2.3.1.2. Primary Sedimentation

Sedimentation is generally the most common method used for mechanical purification where solids are separated by settlement in a settling basin. The particles sink to the bottom, forming a primary sludge that is continuously scraped, pumped or sucked from the basin. Dissolved air flotation, or dispersed air flotation, is another primary treatment seen in pulp and paper mills. Air is bubbled through the wastewater and small bubbles are formed which will attach to the suspended particles and rise them to the surface. Sludge is formed at the surface and removed with help of top scrapers and heavier fractions taken out in the bottom with sedimentation (Hultman, 1997).

Sedimentation tanks are designed to operate continuously. They are usually rectangular or circular and have hoppers for sludge collection. Most sedimentation tanks are constructed with gently sloped bottoms and have sludge hoppers with relatively steep sides. Non-mechanized settling tanks are used only in very small installations. The sludge moves to hoppers by gravity, where it is removed. Primary sedimentation tanks may provide the principal degree of wastewater treatment, or may be used as a preliminary step in further treatment of the wastewater. Sedimentation used as a preliminary step to biological treatment, their function is to reduce the load on the biological treatment units. Efficiently designed and operated primary sedimentation tanks should remove 50 - 65 percent of the suspended solids and 25 - 40 percent of the biochemical oxygen demand. The tank is designed on the basis of average daily flow or daily flow equivalent to the peak hourly flow that requires the largest surface area. Detention time of effluent in the sedimentation tank depends on the tank depth and the overflow rate.
2.3.1.3. Chemical Precipitation

Chemical treatment of wastewater may be advantageous in sedimentation tank. Experience has shown that adding alum, iron or polyelectrolyte at either the primary or secondary clarifier is effective in increasing pollutant removal efficiencies. Lime addition is also effective if the effluent pH is adjusted (by recarbonation or acid addition) to acceptable limits for the subsequent treatment process or for final disposal (Table 2.4).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aluminium salt</td>
<td>Alum (hydrated aluminium sulphate) is the most widely used aluminium salt. It is effective in many wastewater applications but the precipitate sludge is difficult to dewater. The primary use of aluminium salts is for the removal of suspended solids and phosphorus.</td>
</tr>
<tr>
<td>2</td>
<td>Iron salt</td>
<td>Experience has shown that ferric salts are better coagulants than ferrous salts. Both ferrous and ferric salts are effective in the removal of suspended solids and phosphorous, but iron hydroxide carryover in the effluent can affect the effluent quality.</td>
</tr>
<tr>
<td>3</td>
<td>Lime</td>
<td>Lime addition improves grit separation, suspended solids removal, phosphorus removal, and oil and grease removal, as well as reduces odour from dried sludge.</td>
</tr>
<tr>
<td>4</td>
<td>Polyelectrolyte</td>
<td>These are used frequently, by themselves and in conjunction with other coagulant aids, to improve the solids-removal performance of sedimentation units. They are more expensive on a unit-weight basis than the other chemicals in general use, but the required dosage is much lower.</td>
</tr>
</tbody>
</table>

2.3.2. Secondary Treatment

In average strength waste water, the total solids may be classified as being organic or inorganic in origin. In terms of the size of the solids, the distribution is approximately 30% suspended, 6% colloidal and about 65% dissolved solids. The function of primary treatment is to remove as much of the suspended solids as possible. Primary treatment utilizes clarifiers or settling tanks which remove the settable organic and inorganic solids from the waste water.

The effluent from primary treatment therefore contains mainly colloidal and dissolved organic and inorganic solids. Recent effluent standards and water quality standards
require a greater degree of removal of organics from wastewater than can be accomplished by primary treatment. This additional removal of organics can be accomplished by secondary treatment. The secondary treatment process consists of the biological treatment of wastewater by utilizing many different types of microorganisms in a controlled environment (Thompson et al., 2001; Persson, 2011).

In the biological treatment of wastewaters, a mixed population of microorganisms utilizes the colloidal and dissolved organics found in the effluent from the primary treatment as their main food supply. When the oxidation of organics occurs in the presence of dissolved oxygen, the end products include carbon dioxide, water, sulphates, nitrates, and phosphates. The remainder part of the consumed organics is used as building blocks in a series of synthesis (reproduction) reactions that result in an increase population of microorganisms. The biological mass must subsequently be separated from the wastewater to ensure a proper degree of treatment within effluent and water quality standards. Secondary treatment may be aerobic or anaerobic.

2.3.2.1. Aerobic Treatment

Aerobic microorganisms require oxygen to support their metabolic activity. Oxygen is supplied in the form of air by aeration equipment. There are numerous of aerobic systems available for degradation of oxygen-demanding organic compounds in industrial wastewater; aerated lagoons, activated sludge systems, biofilm processes etc. (Persson, 2011).

(i) Aerated Lagoon

One type of biological treatment often used for pulp and paper effluents is the aerated lagoon, which is a large, shallow (≈4m) pond where wastewater is treated biologically with active microorganisms and mechanical aeration. The aerated lagoon is very space consuming because it is dimensioned for a residence time of 5-7 days and consumes a lot of energy for aeration. However, it is very easy to operate and maintain, and the shock load capacity is high. In recent years some aerated lagoons have been converted
into LAS-facilities which are long-term aerated activated sludge treatment plants with a residence time of around one day. Parts of the old aerated lagoon have then been utilized for the aeration and other parts used for temperature stabilization and cooling of hot wastewater effluents. The aerated lagoon primarily removes BOD and can also reduce emissions of AOX to some extent. The removal efficiency is dependent on residence time, pH, temperature, amount of sludge and degree of aeration (Hultman, 1997; Persson, 2011).

(ii) Moving Bed Bioreactor

Several plants have invested in the Moving Bed Bioreactor (MBBR) due to stricter environmental regulations and increase in production. The basin is filled with thousands of suspended plastic carriers that are floating free in a reactor, which have microorganism attached on a film on the carriers. Air is supplied from the bottom of the reactor, which keeps the carriers moving and permits a higher load, a better mixing, and a higher flush. The biggest advantage with a suspended biofilm process is that it does not require return of activated sludge, has very small space requirements, has good shock resistance and can operate at very high concentrations of biomass (Persson, 2011).

(iii) BioFiltration

Another type of biofilm reactor that is used for pulp and paper mill wastewater is the biofilter reactor. The reactor is equipped with a biological filter of a fixed biomass carrier that serves as a filter as well as a biological contactor. Wastewater and air is fed from the bottom of the reactor and led in an upward direction through the dense granular bed. No subsequent clarifier is needed, because all material is retained within the filter, which with time must be cleaned (backwashed). The filter is operated with a hydraulic retention time of around 0.5 h, and very high BOD reductions are seen. The reactor is however only suitable for wastewaters containing low BOD concentrations due to clogging problems at higher concentrations. This treatment is also often used for tertiary treatment, where it functions as a polishing step (Mobius, 2006).
(iv) Activated Sludge Process

Pulp and paper mills that have limited space and sensitive recipients are using the activated sludge (AS) process for biological treatment. The wastewater is treated in two steps; aeration and sedimentation. In the first step, wastewater is treated with a high concentration of microorganism and a powerful aeration, and the retention time can vary between a couple of hours and up to a day. In the second step water and sludge is separated in a sedimentation basin and parts of the sludge is pumped back to the aeration basin. The recirculation of sludge enables a high concentration of microorganisms which is of importance for extensive reduction in organic material. The activated sludge systems are more sensitive than aerated lagoons and cannot stand fast load changes. However, the degree of efficiency can be controlled, and very high BOD-reductions are seen (Thompson et al., 2001; Persson, 2011). In the conventional effluent treatment plant of pulp and paper industry effluent is treated in non specific manner. The conventional biological methods employed in the industry include use of aerated lagoons and activated sludge processes. However, such treatment systems are generally less effective in removing colour, chemical oxygen demand (COD), and chlorinated phenolic compounds (Raj et al., 2007; Saunamaki 1997). Therefore, more advanced alternative biological wastewater treatment strategy is required to meet discharge limits set by regulatory agency. Such biological methods have been found to be more effective and eco-friendly since they are capable of degrading not only lignin but also chloro-organics contributing to AOX. Attempts have been made to decolorize and/or degrade toxicants in pulp and paper mill effluents with fungi and bacteria.

2.3.2.2. Anaerobic Treatment

Anaerobic treatment is a biological process, in which, decomposition of organic matter occurs without oxygen. Two processes were occurred during anaerobic decomposition. In first step, facultative acid forming bacteria use organic matter as a food source and produce volatile (organic) acids, gases such as carbon dioxide and hydrogen sulfide, stable solids and more facultative organisms. In second step, anaerobic methane formers use the volatile acids as a food source and produce methane gas, stable solids. The methane gas produced by the process is usable as a fuel. The methane
former works slower than the acid former, therefore the pH stay constant to slightly basic, to optimize the creation of methane. Anaerobic treatment processes are more suitable for treatment of high strength wastewater such as pulp and paper mills. In the literature, there are a variety of studies on the anaerobic treatability and microbial community of this type of effluents (Poggi-Varaldo et al., 1996; Bajpai, 2000; Ince et al., 2007; Benner and Hodson (1985) did studies using a mixed population isolated from anaerobic compost and found that it could mineralize 2-4% of lignin and 14-22% of kraft lignin under anaerobic conditions at 55°C. Similarly, Colberg and Young, (1985) used a mixed population isolated from activated sludge that was able to degrade low molecular weight lignin in anaerobic conditions. Colberg, (1988) reviewed the degradation of lignin and its degradation products under different anaerobic conditions. Ziomek and Williams, (1989) studied the modification of lignin under sulfate reducing conditions. They found that under those conditions, lignin could be partially depolymerized in its polyphenolic groups and parts of its functional groups were degraded. Pareek et al., (2001) found similar results in experiments using lignin and lignin model compounds under sulfate reducing conditions. The limited research done using anaerobic conditions for colour removal usually focused on the combination of this treatment with aerobic processes. Feijoo et al., (1995) used a combination of fungi and anaerobic bacteria for the decolorization of high molecular weight compounds in kraft pulp effluents. In this study, decolorization was obtained only after fungal pretreatment of the effluent. This pre-treatment in turn enhanced the removal of high molecular weight compounds by 79%. Tezel et al., (2001) studied sequential aerobic/anaerobic treatment of pulp and paper effluents. This combination enhanced the total removal of COD by 91%, AOX by 58%, and colour by 90%. Chuphal et al., (2005) studied the use of anaerobic decolorization followed by aerobic treatment of the effluents. In this case, the author found up to 88% colour reduction while using a three step anaerobic-aerobic sequential reactor. However, it must be observed that only 59% colour reduction was observed in the anaerobic phase and this was supplemented with dextrose as a source of carbon. As was remarked in the cases above, decolorization under anaerobic conditions was achieved. However, the degree of decolorization during the anaerobic phases was not enough for the system to stand on its own in mills with strict colour regulations. While integrated methods is the current trend, a system that
could achieve higher degree of anaerobic decolorization is desired as it will result in a process that requires less energy, produces less sludge, and represents a potential source of energy production.

There are several limitations in anaerobic treatment of pulp and paper industry effluent. Sulphur content in the wastewaters is the main disadvantage for application of anaerobic systems, because one of the end products is hydrogen sulphide in the anaerobic biodegradation in the presence of sulphate (Lettinga et al., 1991). The other important issues for the application of anaerobic treatment in pulp and paper mills are toxicity of wastewater, anaerobic biodegradability characteristic of specific waste types such as lignin derivates, resin and fatty acids, loading capacity, response to loading fluctuation, and recovery of energy and chemicals (Sumathi and Hung, 2006). Some researchers state that bleached effluents are not suitable for anaerobic decolourization due to the low biodegradability and the presence of toxic compounds that can affect methanogens (Pokhrel and Viraraghavan, 2004). Most literature regarding biological decolourization states that lignin degradation does not take place under anaerobic conditions (Feijoo et al., 1995; Kirk and Farrell, 1987). Therefore, anaerobic decolorization of effluents containing lignin chromophores is not expected. Despite these arguments, literature presents cases of lignin degradation using anaerobic treatments.

2.3.3. Tertiary and Advanced Treatment

2.3.3.1. Tertiary Treatment

(i) Chemical

Tertiary and advanced waste water treatment is used to remove specific waste water constituents that cannot be removed by secondary treatment. Different treatment processes are necessary to remove nitrogen, phosphorus, additional suspended solids, and refractory organics or dissolved solids. Sometimes it is referred to as tertiary treatment because advanced treatment usually follows high-rate secondary treatment. However, advanced treatment processes are sometimes combined with primary or secondary treatment (e.g., chemical addition to primary clarifiers or aeration basins to
remove phosphorus) or used in place of secondary treatment (e.g. overland flow treatment of primary effluent).

Some substances that are discharged from pulp and paper mills are very persistent and cannot be removed with secondary treatment alone. As a consequence, a tertiary treatment must be adopted to reduce concentrations of COD, AOX and colour, to meet the increasingly stringent discharge regulations (Jamil et al., 2011, Catalkaya and Kargi, 2007). These substances are then treated with more advanced techniques, for example tertiary biofilters, membrane processes, evaporation, chemical precipitation, flocculation and oxidation processes. Some of these techniques are well known and implemented in real life and others are still elaborated at research level (Ried et al., 2012).

(ii) Precipitation/Flocculation

It is necessary here to distinguish between two different types of chemical treatments; flocculation and precipitation, as they involve different types of purification mechanisms. Flocculation, is based on an addition of ferric ions (Fe$^{3+}$), aluminium ions (Al$^{3+}$) or/and long chained polymers to the effluents. Very small colloidal particles cannot be removed with sedimentation due to a negatively charged surface in water, causing a repellent force. The added metal ions will react with the water to from hydroxides, which in turn adsorb the colloidal particles by sweep coagulation and form larger flocks that easily can settle. The coagulants can also stick to the surface of the colloidal particles and neutralize the local negative surface charge, resulting in colloid destabilization and promote formation of larger particles that can be separated with sedimentation. This type of process is very efficient for removal of fibre residues and colour (Persson, 2011).

Chemical precipitation is a very common and well-known technology, especially for phosphorous removal in municipal wastewater treatment. It involves the addition of metal salts of aluminium, iron or calcium to alter the physical state of dissolved solids and facilitate their removal by sedimentation. The pulp and paper mill effluents do not contain especially high phosphorous concentrations, it is here more of relevance to remove residual phosphorus that might have been added in the biological treatment as
nutrient. The positively charged metal ions will react with the residual phosphorus and resin acids in the wastewater, and form insoluble precipitates, which can be separated from the aqueous phase with sedimentation or flotation (Persson, 2011).

Chemical coagulation, using alum, ferric chloride, ferric sulphate and lime have been studied extensively (Milstein et al., 1988; Beulker and Jekel, 1993; Stephenson and Duff, 1996; Kumar et al., 2011b). During investigation the batch flocculation process on diluted black liquor effluent with initial COD and BOD of 7000 mg/L and 1400 mg/L respectively, found that Poly Aluminium Chloride (PAC) as flocculation agent reduced COD to 84%. Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has grown rapidly (Sarika et al., 2005; Ebeling, 2005). Acrylamide is a crystalline and relatively stable monomer which is soluble in water and many organic solvents. Acrylamide is a polyfunctional molecule that contains a vinylic carbon–carbon double bond and an amide group. The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels–Alder and free radical reactions (Girma et al., 2005). The flocculations of the suspended particles occur via the double bond. Polyacrylamide (PAM) is commonly used as a polymeric flocculant because it is possible to synthesize polyacrylamides (PAMs) with various functionalities (positive, neutral or negative charge) which can be used to produce a good settling performance at relatively low cost.

The advantage of polymeric flocculants is their ability to produce large, dense, compact and stronger flocs with good settling characteristic compared to those obtained by coagulation. It can also reduce the sludge volume. Furthermore, the polymer performance is less dependent on pH. There are no residual or metal ions such as Al\textsuperscript{3+} and Fe\textsuperscript{3+}, were added and hence the alkalinity is maintained. The flocculation performance of flocculants primarily lies on the type of flocculant and its molecular weight, ionic nature and content, on the suspension content in the wastewater and the type of wastewater (Qian et al., 2004) The use of polymeric flocculants or polyelectrolytes, especially those of high molecular weight, has resulted in tremendous performance improvement for industrial separation processes (Zhong et al., 2003; Walker and Kelley, 2003). According to Ovenden and Xiao, (2002), a good clay flocculation is observed when colloidal alumina (cationic micro particles) is used in
conjunction with cationic and non-ionic PAMs but a synergetic effect is observed in conjunction with anionic PAM. Recently, a photometric dispersion analyzer (PDA) was successfully applied to monitor a flowing suspension of papermaking filler flocculated by cationic polymer and microparticle system (Wang et al., 2006). Although chemical treatment show good results, the treatment has associated drawbacks like dewatering and disposal of the generated sludge.

(iii) Adsorption

Adsorption has been found to be an efficient and economic method to remove dyes, pigments and other colorants and to control the bio-chemical oxygen demand. Activated carbons, inorganic oxides, natural adsorbents (such as clays and clay minerals, cellulose materials, chitin, and chitosan) have been extensively used as adsorbents to treat wastewaters (Al-Asheh et al., 2003; Naseem and Tahir, 2001). It is advantageous to use small amount of adsorbent with large surface area (Marquez and Costa, 1996; Marmagne and Costa, 1996). Different types of adsorbents derive from different sources can be used to adsorb specific adsorbate or target compounds. The best adsorbent for a specific target compound can be selected based on higher adsorption capacity of the adsorbents for target solute to be removed.

The heat treatment of coal between 700°C and 800°C is popularly known as carbonization. This includes coking, charring and reaction with oxidizing gases such as oxygen, carbon dioxide and water vapours. The process enhances the carbon content percentage and introduces pores. The product so obtained is known as activated carbon. Activated carbon adsorption is considered very effective in the reduction of colour, adsorbable organic halides (AOX) and the non-biodegradable fraction of the pulp mill wastewater. Some other materials like organic flocculant (Marwichem DEC), powdered activated carbon (PAC), bentonite, activated clay and commercial synthetic inorganic clay (macrosorb) were used for the activated sludge laboratory pilot plant model (Pala and Tokat, 2002). Carbonized coal adsorption process is proved to be an attractive and effective process in wastewater treatment for removing colour, heavy metals and other toxic compounds (Matisova and Skrabakova, 1995).
Despite its prolific use in water and wastewater industries, commercial activated carbon remains an expensive material. This has led to search for low-cost materials as alternative adsorbents in order to remove phenolic and lignin compounds (Montgomery, 1985; Bailey et al., 1999; Mehmet and Ahmet, 2005). Sepiolite is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels, having the ideal structural formula $\text{Si}_{12}\text{Mg}_{8}\text{O}_{30}(\text{OH})_{4}(\text{OH})_{2}(\text{OH})_{2}$ for the half-unit cell (Brauner and Preisenger, 1956). Sepiolite has a common industrial application due to its molecular sized channels and large specific surface (more than 200 mg). It is an effective sorbent in the removal of compounds, such as aromatic amines, diquat, paraquat and methyl green from aqueous solutions (Sabah et al., 2002; Rytwo et al., 2002). Fly ash was extensively used as an adsorbent material for removing various heavy metals and colours of organic compounds (Mott and Weber, 1992; Viraghavan and Alfaro, 1998). It was reported that the carbon content of fly ash plays a significant role during the sorption of organic compounds. In addition, fly ash and volcanic ash were used to remove phenolic compounds from polluted surface waters and wastewaters (Banerjee et al., 1997; Kao et al., 2000).

High removal of colour by activated charcoal, fuller’s earth, and coal ash was reported by Murthy et al., 1991. Shawwa et al., (2001) also showed that high removal of colour, COD, DOC, and AOX from bleaching wastewater by activated coke. Problems associated with the use of adsorption materials include long contact time as well as competitive interaction between different adsorbates and adsorbent. In addition, these adsorbents must be regenerated (reused) for the process to be economically feasible.

A comparison between activated charcoal and heat-treated coal for decolourization of pulp and paper mill waste water was studied. The heat-treated coal was prepared in an inert atmosphere at 800°C. The study showed that heat-treated coal is a suitable adsorbent and can be used for the decolourization of pulp and paper mill effluent streams (Mishra et al., 2008).

The organic compounds such as chlorophenols are not fully degraded by biological processes which require advanced oxidation after biological treatment to reduce refractory organics and colour of the pulp mill wastewater.
(iv) Membrane Filtration

Membrane treatment in pulp and paper industry serves to optimize loop closure and therefore helps to reduce fresh water intake as well as wastewater treatment. Other purposes of membrane processes are: improved product quality because of lowered pollution of loop water, re-use of treated effluent in production, recovery of valuable substances e.g. coating pigments and minimizing environmental impact because of improved effluent quality. Ultrafiltration (UF) and reverse osmosis are some examples of membrane filtration technology for removal of colur. Usually, they have been used to remove high molecular weight dissolved organic components from mills effluent streams. The filtration techniques are now being used for the removal of colour and to further reuse process wastewaters of this industry (Joensson et al., 1996; Katkar and Sasidharan, 2000; Laitinen et al., 2001). Membrane techniques usually represent a large capital investment. This process requires pre-treatment in order to prevent problems of fouling.

The treatment of pulp and paper effluent by means of UF is an attractive method, as most of the polluting substances consist of high molecular mass compounds that are readily retained by UF (Guangli et al., 2004; Sierka et al., 1997). Ultrafiltration treatment of E-stage effluent can result in 70–98% removal of colour, 55–87% removal of COD and 35–44% reduction in biological oxygen demand (Gerbasi et al., 1993; Guangli et al., 2004). The flux decline caused by the “irreversible adsorption of foulants”, as in many other UF applications, is a major obstacle to the economic implementation of UF for the purification and recycling of this type of wastewater. Flux decline leads to an increase in membrane cleaning costs, process down time and in some instances, even membrane damage as result of the frequency and harshness of cleaning conditions (Sierka et al., 1997; Maartens et al., 2002). In one study Oliveira et al., (2009) showed that effluent treatment by ultrafiltration was technically feasible and the treated white water had good potential to be reused in some processes in the paper industry. Amaral et al., (2008) used microfiltration (MF) combined with a membrane bioreactor (MBR) for the treatment of bleach pulp mill effluents. The results showed that the use of the MF-MBR system was an excellent alternative for the treatment of bleach pulp mill effluents with an average COD removal of 95% (Hong et al., 2007).
2.3.3.2. Advance Treatment

Advanced oxidation processes (AOP) are among promising technologies that have received interest for the treatment of pulp and paper bleach effluents. AOPs are used to oxidize complex organic constituents of wastewater that are difficult to degrade biologically into simpler end products. Advanced oxidation processes (AOPs) are based on the generation of very reactive non-selective transient oxidizing species such as the hydroxyl radicals (OH•), which were identified as the dominant oxidizing species (Al-Rasheed, 2005). The most common advanced oxidation processes are H₂O₂, UV/O₃, O₃, Fenton’s reagent UV/H₂O₂ and photochemical processes (Metcalf and Eddy, 2004; Maria, 2013).

(i) Ozone

Ozone is a strong oxidising gas and it reacts with inorganic and organic compounds directly or indirectly via the formation of hydroxyl radicals. It preferentially oxidises electron-rich molecules containing carbon–carbon double bonds and aromatic alcohols. The ozone treatment splits the long-chain compounds making them biodegradable. The combination of ozonation and aerobic biotreatment is demonstrated to be an effective method for destroying lipophilic extractives and hence increases the biodegradability of pulp mill processed water before returning them to the biotreatment unit (Kamenev, 2003).

Several studies have also been published on ozone pre-treatment prior to membrane filtration. These studies have shown a decrease in the use of membrane fouling when the filtered effluent was first degraded by ozone. However, in many cases, the permeate purity also decreased because of an increase of degraded smaller compounds that could be permeated through the membrane (Park, 2002; Schlichter et al., 2003; Bes-Pi et al., 2004; Karnik et al., 2005; Leiknes et al., 2005). As discussed above, ozone treatment and membrane filtration have both been used for effluent treatment in combination with biological treatment in the pulp and paper industry. Ozonation is one of the most effective methods, which have been shown by many authors (Hostachy et al., 1997; Zhou and Smith, 1997; Yamamoto, 2001; Freire et al., 2000).
(ii) Fenton’s Reagent

Almost every method used resulted in some degree of colour removal from the pulp mill effluent. However, the Fenton’s reagent utilizing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ resulted in the highest colour, TOC and AOX removals under acidic conditions when compared with the other tested AOPs. Approximately, 88% TOC, 85% colour and 89% AOX removals were obtained in 30 min by the Fenton’s reagent at pH 5. The photo-fenton process yielded comparable removal of TOC (85%), colour (82%) and AOX (93%) within 5 min due to oxidations by UV light in addition to the Fenton’s reagent. The fast oxidation reaction by the photo-Fenton treatment makes this approach more favourable when compared with the others (Catalkaya and Kargi, 2007). Fenton and photo-fenton reactions are highly effective for the treatment of bleaching kraft mill effluent (Perez et al., 2002).

(iii) Photocatalysis

Photocatalysis, an advance oxidation process, is an important alternative because it can cause the complete mineralization of a wide range of organics without any harmful environmental impact (Ahmed et al., 2010). When a photon of light strikes the catalyst surface, an electron is raised from the valence band to the conduction band (Kansal et al., 2007). It can oxidize a wide range of adsorbed pollutants either directly or by producing OH$^-$ radicals (from $\text{H}_2\text{O}/\text{OH}^-$ ion), which can also oxidize organics non-selectively. The addition of $\text{H}_2\text{O}_2$ to the photocatalytic system increases the degradation positively because it can additionally form OH$^-$ radicals either by direct radiation absorption or by accepting conduction band electrons, (Rodrigues et al., 2008).

The TiO$_2$ assisted photocatalysis has been efficiently utilized for the remediation of pulp and paper mill effluents during the recent years. Perez et al. (2001) investigated that photocatalysis is efficient for the reduction of AOX (Adsorbable Organic Halides) (95%), TOC (Total Organic Carbon) (50 %), total phenols, and toxicity from the bleaching effluent. Boyd and Almquist, (2008) found out that photocatalysis with TiO$_2$ is an effective method for the degradation of COD (Chemical Oxygen Demand) and toxicity from pulp and paper mill effluents.

TiO$_2$-assisted photo-catalysis (UV/TiO$_2$) resulted in the highest TOC and toxicity removals under alkaline conditions when compared with the other AOPs tests.
Approximately, 79.6% TOC and 94% toxicity removals were obtained by the TiO$_2$-assisted photo-catalysis (UV/TiO$_2$) with a titanium dioxide concentration of 0.75 g/l at pH 11 within 60 min. (Catalkaya and Kargi, 2008).

The heterogeneous photocatalytic systems (UV/semiconductors) have been extensively studied due to their ability to photosensitize the complete mineralization of a wide range of organic substrates at ambient temperatures and pressures, without the production of harmful by-products, including phenols, amides, aromatics, dyes and pesticides (Serpone and Pelizzetti, 1989; Fox and Dulay, 1993; Khodja et al., 2001; Kansal et al., 2007; Lathasree et al., 2004; Kusvuran et al., 2005). Titanium dioxide (TiO$_2$) was found to be a more efficient catalyst than other semiconductors for the photocatalytic degradation of pollutants due to faster electron transfer to molecular oxygen (Fujishima et al., 2000). The use of TiO$_2$ has recently been reported for photocatalyzed mineralization of chlorinated hydrocarbons (Noorjahan et al., 2003; Alhakimi et al., 2003). However, widespread use of TiO$_2$ is uneconomic for large-scale water treatment operations. Daneshvar et al., (2003) reported that ZnO appears to be a suitable alternative to TiO$_2$ since its photodegradation mechanism has been proven to be similar to that of TiO$_2$. The pre-treatment of pulp and paper mill wastewater by the oxidation process has been reported by different researchers (Noorjahan et al., 2003; Mansilla, 1997 et al.,; Torrades et al., 2001).

Torrades et al., 2001 applied photocatalysis alone and in combination with ozonation for the treatment of bleach plant effluents. Fairly concentrated effluent samples were treated by sequences of photocatalysis and ozonation or by simultaneous application of both techniques. The effect of a composite TiO$_2$/ZnPC (titanium dioxide/zinc phthalocyanine) system for treatment of real effluent and lignosulphonate has been studied by Machado et al., (2003). Yeber et al., (2000) investigated the decolorization and acute toxicity reduction of a bleaching effluent by photocatalysis using TiO$_2$ and ZnO. Efficiency of ZnO has been reported to be particularly noticeable in the photooxidation of pulp mill bleaching effluent (Peralta-Zamora et al., 1998) and textile mill wastewater (Daneshvar et al., 2003). Balcioglu and Cecen, (1999) observed that wastewaters treated by photocatalysis enhanced the biodegradability of remaining pollutants in bleach plant effluent, the effectiveness of photocatalysis was strongly affected by the initial COD and
chloride ion concentrations, and that photo catalysis is significantly more effective on pre-treated waters than on raw or untreated wastewaters. Perez et al., (1997) found that the TOC of laboratory generated bleach effluent decreased from approximately 300 mg/l to less than 50 mg/l after 20 h in the photocatalytic reactor. The solar/UV photocatalytic water detoxification is identified as a promising technology to be used in solving severe problems. (Amat et al., 2005) discussed the solar photocatalytic process to remove paper mill wastewater pollutants and reported that wastewaters from industries having high COD values are effectively degraded by photo catalytic methods.

(iv) Electrochemical

Electrochemical processes can be applied in various configurations such as electro oxidation, electro precipitation, electro coagulation, electro deposition, electro-Fenton, etc. Using three-dimensional electrodes with a Ti/Co/SnO$_2$–Sb$_2$O$_5$ anode to treat paper mill wastewater, Wang et al., (2007) reported that pH and current density had a significant effect on the total COD and colour removal efficiency. Electrochemical degradation of pulp and paper waste-water has been reported by few researchers. Ugurlu et al., (2008) studied electro coagulation as a post-treatment of pulp and paper effluent using aluminium anodes in a batch electrochemical cell and reported removal capacities of 80% for lignin, 98% for phenol, 70% for BOD and 75% for COD. Mahesh et al. (2006) studied the electrochemical degradation of pulp and paper mill effluent by electro-coagulation in a batch cell followed by chemical flocculation and reported an overall COD removal of 91% and almost complete colour removal. Mansour et al., (2007) studied the treatment of waste-water in the paper industry by coagulation followed by electro-flotation and reported more than 95% removal of suspended solids. Patel et al., (2008) and Pooppana et al., (2009) had studied the effect of electrochemical treatment of pentachlorophenol in pulp bleaching effluent.

(v) Combined Advance Oxidation Process

Advance oxidation such as ozonation, photo-fenton oxidation chemical coagulation-flocculation and activated carbon adsorption and membrane filtration has been used by various researchers for the treatment of pulp and paper industry effluent. According to
the literature each of these techniques are capable of removing different compounds from effluent. Therefore the application of two or more such treatment techniques has a higher capability for removing a variety of compounds. Hence the combination of these techniques is another option to treat Kraft pulp mill effluent which contains several compounds.

The combined process of UV/Hydrogen peroxide photocatalysed by Titanium dioxide showed the COD, colour and AOX reduction by 76%, 78% and 45% respectively (Subashini, 2013). A study on the treatment of Kraft pulp mill effluent by ozonation alone, and by combined treatment of ozonation preceded by chemical coagulation, activated carbon adsorption or membrane filtration has been conducted. When ozonation was conducted alone, more than 70% of colour and phenolic compounds got reduced. When ozonation was preceded by chemical coagulation or powdered activated carbon adsorption, more than 90% reduction of phenolic compounds could be achieved at similarly low pH.

The technical and economic feasibility of large-scale operations using other treatment alternatives such as adsorption, wet oxidation, ozone treatment, fractional precipitation, ultrafiltration, combined biological and membrane based treatments, etc. are questionable. Major limitations of the above listed physico-chemical methods are cost and generation of secondary pollutants.

**(vi) Combined Biological and Physicochemical Treatment**

Biologically treated effluents still contain significant amounts of colour compounds, micro-organisms, recalcitrant organics and a minor amount of biodegradable organics as well as suspended solids. Biological treatment does not significantly reduce the inorganic content in the effluent and desalting may be needed before reuse of the effluents in the manufacturing processes. Fontanier et al., (2005) simulated concentrations in the pulp mill water circulations and showed that recycling of biologically treated effluent back to process water caused an increase in the concentration of impurities. However, the replacement of fresh water in the bleaching and pulp washing stages by effluent treated by catalytic ozonation (COD content 24 mg/L) resulted in COD levels close to the original process values. Some mill-scale NF
(nanofiltration) and reverse osmosis (RO) membrane filtration plants have been installed in the pulp and paper industry to purify tertiary effluent from external biological treatment processes. For instance, in 1999 Eltmann newsprint mill of Papier fabrik palm installed spiral wound nanofiltration (NF) to reduce COD, AOX and colour in their effluents. Prior to NF the effluent is biologically treated (activated sludge plant) and pre-filtered using sand filters.

Mohamad et al., (2008), used granular activated carbon – sequencing batch bio-film reactor (GAC-SBBR) for the treatment of wastewater of recycled pulp and paper mill. The results indicated that the biofilm attached onto granular activated carbon (GAC) can substantially remove recalcitrant organics in the wastewater, within the range of 10 – 100% AOX removal depending on the selected HRTs. Afzal et al., 2008, used Pilot scale reactor based on combined biological–coagulation–filtration for the treatment of effluent from a paper and board mill. Biological treatment by fed batch reactor (FBR) followed by coagulation and sand filtration (SF) resulted in a total COD and BOD reduction of 93% and 96.5%, respectively. A significant reduction in both COD (90%) and BOD (92%) was also observed by sequencing batch reactor (SBR) process followed by coagulation and filtration. In a study by Assalin et al., 2009, the treatment of paper mill effluent for COD, TOC, total phenols and colour removal was investigated using combined activated sludge-ozonation processes and single processes. The combined activated sludge-O3/pH 10 treatment was able to remove around 80% of COD, TOC and colour from Kraft E1 effluent. For the total phenols, the efficiency removal was around 70%. The ozonation post treatment carried out at pH 8.3 also showed better results than the single process. The COD, TOC, colour and total phenols removal efficiency obtained were 75.5%, 59.1%, 77% and 52.3%, respectively. A treatability study of industrial wastewater containing chlorinated nitro aromatic compounds (CNACs) by a catalytic ozonation process (COP) with a modified Mn/Co ceramic catalyst and an aerobic sequencing batch reactor (SBR) was investigated. The performance of SBR to treat COP effluent was also examined. At an organic loading rate of 2.0 kg COD/(m$^3$·d), with hydraulic retention time (HRT)=10 h and temperature (30±2) °C, the average removal efficiencies of NH3-N, COD, BOD5, TOC, and colour in a coupled COP/SBR process were about 80%, 95.8%, 93.8%, 97.6% and 99.3%,
respectively, with average effluent concentrations of 10 mg/L, 128 mg/L, 27.5 mg/L, 25.0 mg/L, and 20 multiples, respectively (Bing et al., 2010).

Dhir et al., (2012) evaluated the effect of integrated solar assisted advanced oxidation process (AOP) and biological treatment on the extent of degradation of effluents from chlorination (C) and first alkaline extraction (E1) stages of soda pulp bleaching in agro-residue-based pulp and paper mill. The biological treatment (24 h) of C and E1 effluent resulted in 30 and 57 % of degradation, respectively. Solar-induced AOP of C and E1 effluents resulted in 53 and 43 % degradation under optimized conditions (2.5 g L⁻¹ ZnO at pH 8.0) after 6 h of exposure.

2.4. Biological Approach by using Fungi and Bacteria

By using activated sludge process which is commercially used at mill sites the industry was not able to control the water pollution in the current scenario. This technology was not successful to attain the standards provided by the government agencies because of the presence of non specific microbes in the activated sludge. The waste water of the pulp and paper industry contains specific compounds such as lingo cellulose, for the treatment of such pollutant specific microorganisms were required. Therefore, the researchers were focusing on the treatment of pulp and paper wastewater by using specific microorganisms.

2.4.1. Fungal Treatment

Fungi are most attractive for lignin degrading microorganisms. Research has been focused on biotechnological approaches with white-rot fungi due to their powerful lignin-degrading enzyme systems (Haddadin et al., 2002). Among them, Phanerochaete chrysosporium (Yin et al., 1989; Zouari et al., 2002; Bajpai and Bajpai, 1994), Lentinus edodes (Esposito et al., 1991; Wu et al., 2005), and Trametes (Coriolus) versicolor (Martin and Manzanares, 1994; Modi et al., 1998) have been reported to be effective in reducing the various pollution parameters of the Kraft bleach plant effluents.

White rot fungi are used for bioremediation processes because these organisms have the ability to degrade a wide range of environmental pollutants (Lankinen et al., 1990).
et al., 2001 reported that white rot fungi are the ideal organisms for decolorization, reduction of absorbable organic halides and chemical oxygen demand. The decolorization can be achieved either by adsorption or oxidative degradation by the enzymes. Several strains of white rot fungi have been found to decolorize wood processing wastewater. Luciana et al., (2003) developed a MYCOR (Mycelial colour removal) process for the treatment of spent chlorine bleaching liquor using *Phanerochaete chrysosporium* in rotating biological contractor. The MYCOR process efficiently reduces the amount of toxic low molecular weight in the effluent. The immobilized mycelium of *Phanerochaete chrysosporium* on the surface of polyurethane foam can be used for the treatment of bleach plant effluents by the trickling filter reactor called the MYCOPOR process. Lankinen 1990 reported that *Phanerochaete chrysosporium* produces iso-enzymes including lignin peroxidase (LiP), manganese dependant peroxidase (MnP) which is capable of degrading chlorinated compounds in pulp bleaching effluents. *Phanerochaete chrysosporium* is also used by Christov and Driessel, 2003 for the waste water bioremediation in pulp and paper industry. Selvam et al., 2006 reported the decolourization and dechlorination of pulp and paper industry effluent by *Thelephora sp*. In a study by Celine Justino et al., in 2011, they had used fungal strains *Rhizopus oryzae* and *Pleurotus sajor caju*, for decolourization of paper industry effluent. This study was compared with enzyme (laccase) and oxidation process (photo-Fenton) as tertiary treatments. Tertiary treatments by *Rhizopus oryzae* and photo- Fenton oxidation were able to remove phenol completely from the effluent samples whereas *P. sajor caju* and laccase were able to remove 60–85% of the phenol. Belem et al., 2008 ; Prasongsuk et al., 2009 reported the decolourization of pulp mill wastewater using thermotolerant white rot fungus *Daedaleopsis sp*. Michael et al., 1991 reported purified lignin peroxidase and manganese peroxidase were effective in the decolourization of Kraft bleach plant effluent.

Lokeshwari et al., (2013) used *Aspergillus flavus*, white rot fungi which was isolated from pulp and paper effluent for decolourization and detoxification of pulp mill effluent and showed 94% lignin degradation after 8 days. Black liquors from a soda pulping mill were treated with the white-rot fungus *Trametes versicolor* to detoxify and reduce colour,
aromatic compounds and chemical oxygen demand (COD). Reductions in colour and aromatic compounds of 70–80% and in COD of 60% were achieved (Xavier Font et al., 2003). Kumar et al., (2010) used fungal strain RV.F1.90 for decolourization of pulp mill effluent and showed that the colour reduction was proportional to the decrease in concentration of kraft liquor and commercial lignin. Result showed 94% colour removal. Rhizopus oryzae, a zygomycete, was found to decolorize, dechlorinate, and detoxify bleach plant effluent this study was reported by Nagarathnamma and Bajpai, 1999. This fungus removed 92 - 95% of the colour, 50% of the chemical oxygen demand, 72% of the adsorbable organic halide, and 37% of the extractable organic halide in 24 hr. Singhal and Thakur (2009), isolated three fungal strains from sediments of pulp and paper mill and used for decolourization of effluent. The results showed significant reduction in colour, lignin and toxicity of the effluent. Naghdi et al., (2013) exploited rainbow fungus i.e., Coriolus versicolor for bioremediation of bagasse soda pulp bleaching effluent containing chlorinated organic compounds. Sehanat et al., (2009) used white rot fungi, P. chrysosporium and Daedaleopsis sp. for decolourization of wastewater of pulping process and showed decolourization of wastewater 52% and 86%. The percentage reduction in COD of effluent was 66–83%.

Combinations of fungal species and bacterial strains were also studied by many researchers. In a study Singh and Thakur, (2005) showed the reduction in colour (70%), lignin (25%), COD (42%), AOX (15%) and phenol (39%) by using sequential anaerobic and aerobic treatment in two steps. The anaerobically treated effluent was separately applied in bioreactor in presence of fungal strain, Paecilomyces sp., and bacterial strain, Microbrevis luteum and results were found reduction in colour (95%), AOX (67%), lignin (86%), COD (88%) and phenol (63%) by Paecilomyces sp., whereas M. luteum showed removal in colour (76%), lignin (69%), COD (75%) AOX (82%) and phenol (93%) by day third when 7 days anaerobically treated effluent was further treated by aerobic microorganisms.

In another study, different strains of fungi were mixed by Selvam et al., (2011). They used three fungal sp. Polyporus hirsutus, Daedalea flavida, Phellinus sp for bioremediation of pulp and paper mill effluents on laboratory scale and pilot scale. On the laboratory scale a maximum decolourization of 62.2 % and the estimated inorganic
chloride was 820 mg/l by *Phellinus sp* on 10th day of treatment. The achieved reduction in chemical oxygen demand (COD) was reduced to 3010 mg/l (42.1%). In pilot scale, *Polyporus hirsutus* was used and the maximum decolourization of 66.2% was achieved by on 10th day, inorganic chloride 582 mg/l (105%) was liberated and the chemical oxygen demand (COD) was reduced to 3260 mg/l (37.3%). In a study by Xavier *et al.*, (2003) black liquors from a soda pulping mill were treated with the white-rot fungus *Trametes versicolor* to detoxify and reduce colour, aromatic compounds and chemical oxygen demand (COD). The fungus was used in the form of pellets in aerated reactors (fluidized, stirred and air-pulsed reactors). Reductions in colour and aromatic compounds of 70–80% and in COD of 60% were achieved. Kannan, (1990) used three fungi *Polyporus hirsutus, Daedalea flavida, Phellinus sp*, for the treatment of paper industry effluent. In particular their potentials in decolourization, the reduction of the COD and the increase in the inorganic chloride content were analyzed (Selval *et al.*, 2011).

A consortium of two or more fungal species can provide distinct advantage as the species can collectively carry out the treatment process more efficiently. In an another study, (Thakur, 2004; Malaviya and Rathore, 2007) two basidiomycetous fungi (*Merulius aureus* syn. *Phlebia sp*. and an unidentified genus) and a deuteromycetous fungus (*Fusarium sambucinum* Fucke MTCC 3788) were immobilized on nylon mesh and the consortium was used for bioremediation of pulp and paper mill effluent in a continuously aerated bench-top bioreactor. The treatment resulted in the reduction of colour, lignin and COD of the effluent in the order of 78.6%, 79.0% and 89.4% in 4 days. Thakur, (2008) used combination of eight fungal and three bacterial isolates collected from decomposed wood, sediment core and effluent of pulp and paper mill were evaluated for their ability to decolourize kraft pulp bleached effluents.

Various effects of paper mill effluents, including decolorization by white-rot and other fungi, have been reviewed (Garg and Modi, 1999; Garg and Tripathi, 2011; Tripathi *et al.*, 2007). However, the main constraint in using a fungal degrading system is the requirement to maintain growth and/or enzymes (ligninases) activity at the prevailing low pH (4–5). However, at low pH, the solubility of high molecular weight fragments that are derived from lignin is reduced. Furthermore, the natural pH of pulp–paper mill effluent is alkaline (pH 8–9). Therefore, any requirement to reduce the pH to the acidic
range prior to fungal augmentation would be uneconomical (Raj et al., 2007). Considering the above and other facts, bacterial treatment systems that have an optimum pH range of 7–9 may play a pivotal role in biodegradation of pulp and paper mill effluents, without any prior requirement of pH adjustment.

2.4.2. Bacterial Treatment

Lignin modification and degradation have been most extensively studied in wood-rotting basidiomycetes (Hatakka, 1994). White-rot fungi are known to secrete several types of extracellular oxidative enzymes, namely laccases, lignin peroxidases (LiPs), manganese peroxidises (MnP), and versatile peroxidases, which have the capacity to mineralize lignin (Bugg et al., 2011b; Hatakka, 1994). Owing to the fact that fungal enzymes are often less robust in terms of thermal and pH stability, can be costly to produce, and are difficult to optimize by protein engineering, the application of fungal enzymes to lignin depolymerisation has not yet been commercialized (Bugg et al., 2011a).

Bacteria are worthy of being studied for their lignolytic potential due to their immense environmental adaptability and biochemical versatility. There is wide range of examples where bacteria like Pseudomonas aeruginosa, Serretia marcescens, Nocardia, Arthrobacter, Flavobacterium, Micrococcus, Xanthomonas have been identified as lignocellulosic-degrading microorganisms. (Kalyani et al 2008) These include various environmental niches like compost soil, rhizosphere soil, cow dung, lake water containing decomposing plant material, decaying bark and also termite gut where bacteria may be present involved in lignocellulosic degradation as symbionts. (Yang J. et al 2006) (Bugg et al., 2011a; Chen et al., 2012; Santhanam et al., 2011; Vicuna, 1988; Zimmermann, 1990).

In comparison to fungal lignin degrading enzymes, the bacterial enzymes implicated in lignin breakdown are much less well studied. It has been suggested that bacteria might use similar types of extracellular lignin-degrading enzymes to deconstruct lignin (McLeod et al., 2006; Ramachandra et al., 1988). In particular, bacterial laccases are thought to play a role in lignin degradation (Bugg et al., 2011a). Laccases are a class of oxidizing enzymes that can catalyze a multitude of reactions, including the degradation
of polymers, oxidative coupling of phenolic compounds, aromatic ring cleavage and functionalization of polymers (Santhanam et al., 2011). Laccases can depolymerize lignin directly or via the oxidation of smaller mediator molecules, either natural compounds or reagents such as 2,20-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and hydroxybenzotriazole (HBT). In the paper industry, delignification of paper pulp with a laccase-mediator system has been performed in pilot-scale facilities (Morozova et al., 2007).

Analysis on prokaryotic genomes suggested that laccase like enzymes may be widespread in bacteria (Alexandre and Zhulin, 2000; Sharma et al., 2007). Laccase-like genes or activity have been found in several bacterial strains, including Bacillus halodurans (Ruijssenaars and Hartmans, 2004), Bacillus licheniformis (Koschorreck et al., 2008), Bacillus subtilis (Martins et al., 2002), Escherichia coli (Roberts et al., 2001), γ-proteobacterium (Singh et al., 2007), Thermus thermophilus (Miyazaki, 2005), and Streptomyces (Arias et al. 2003; Endo et al. 2003). Bacteria with lignin-degrading ability and the characterization of bacterial lignin-degrading enzymes have significant potential benefits for bioremediation of pulp and paper industrial effluent, contains mainly lignocellulosic compound.

Various reports are available on treatment of pulp and paper mill effluent by using bacteria. Vora et al., (1988) have reported that many bacteria, viz., Pseudomonas, Flavobacterium, Xanthomonas, Nocardia, Aeromonas, Arthrobacter sp., are able to utilize several lignocellulosic compounds of the bleached plant effluent, including organochlorine constituents. Several bacterial species capable of metabolizing various wastewater pollutants have been isolated from the natural environments, viz., Bacillus sp., Bacillus subtilis, Bacillus cereus (Andretta et al., 2004; Chandra et al., 2006, 2009; Mishra and Thakur, 2010; Niazi et al., 2001; Raj et al., 2007; Tripathi et al., 2011; Tripathi and Garg, 2010), Pseudomonas sp., Pseudomonas veronii, Pseudomonas fluorescens, Pseudomonas aeruginosa (Chauhan and Thakur, 2002; Nam et al., 2003; Premutha and Rajkumar, 1994; Shah and Thakur, 2003; Thakur et al., 2002), Arthrobacter chlorophenolicus A6 (Agneta et al., 2004), Serratia marcescens, Citrobacter sp., and Klebsiella pneumoniae (Chandra et al., 2011).
Bacteria isolated from compost soil, viz. *Azotobacter* and *Serratia marcescens*, were capable of degradation and decolorization of lignin (Morii *et al.*, 1995). Bacteria such as *Bacillus subtilis* and *Bacillus sp.* have also been tested for kraft-lignin degradation (Hanafy *et al.*, 2008; Elsalam and Hanafy, 2009). Previously, three potential bacterial strains of *Pantibacillus sp.* *Aneurinibacillus aneurinilyticus* and *Bacillus sp.* were isolated from pulp paper sludge for degradation and decolorization of synthetic lignin at 500 mg/l and characterized their metabolic products by GC–MS analysis (Chandra *et al.*, 2007; Raj *et al.*, 2007; Chandra *et al.*, 2011) and it was observed that lignin does not serve as a growth substrate (Keyser *et al.*, 1978). Lignin degradation is therefore, dependent on the presence of a readily metabolizable co-substrate such as glucose (Hammerli *et al.*, 1986). But increased carbohydrate supply stimulates, while increased nitrogen inhibits, lignin degradation (Garg and Modi, 1999). Therefore, the C/N ratio has been considered a better predictor of lignin degradation than the absolute levels of carbohydrates and nitrogen (Reid, 1979). An important task for effluent treatment is the isolation and characterization of efficient microorganisms together with designing and optimization of process parameters to deal with specific environmental pollutants (Singh and Thakur, 2004; Garg *et al.*, 2011).

In this chapter I have discuss the pulp and paper industry in detail. All the sections including history, raw material used, manufacturing process, the conventional methods available for the treatment of the wastewater and finally the drawbacks of the technologies developed. The researchers are deviating there mind towards the biological approach. The work is going on in this sector from years. But, till date no successful technology have been developed which can treat the pulp and paper waste water holistically.

Keeping all the shortcomings in mind I have designed biological strategy by using bacteria described in my later chapters to develop such a technology which is cost effective, less time consuming, eco-friendly and most important able to treat the pulp and paper waste water and bring down wastewater parameters within the permissible discharge limits.