CHAPTER 3
COLLECTION OF EFFLUENT SAMPLES FROM PULP AND PAPER MILL AND CHARACTERIZATION FOR POLLUTION LOAD

3.1. Introduction

Pulp and paper industry uses tremendous amounts of natural resources and energy in paper manufacturing processes. The pulp and paper industry has been associated with a variety of potential environmental problems, due to the high chemical diversity of the organic pollutants in the effluent. The discharged water effluent contains significant amounts of toxic substances, which can cause death to the living organisms in receiving waters bodies. Various studies had reported the toxic/lethal effects of the released wastewater from pulp and paper industry on the fishes (Owens et al., 1994; Hickey and Martin, 1995; Yen et al., 1996; Vass et al., 1996; Liss et al., 1997; Lindstrom-Seppa et al., 1998; Leppanen and Oikari, 1999; Johnsen et al., 1998; Erisction and Larsson, 2000; Schnell et al., 2000; Kovacs et al., 2002). The effluents can also cause thermal impact, slime growth, scum formation, and loss of aesthetic beauty of the environment. (Pokhrel and Viraraghavan, 2004)

There are three most polluting units in pulp and paper sector i.e. pulping, bleaching and papermaking. The effluent characteristics of these three units are entirely different due to the varying chemical processes involved.

Pulping is the major source of environmental pollution. Effluent generated from pulping unit is called black liquor. It is the most significant and troublesome source of pollution. Black liquor consists of various wooden compounds such as lignin, cellulose, hemicellulose and extractives. It also contains some chemicals such as, sodium hydroxide, sodium carbonate, sodium sulphide and bisulfites. These types of molecules are very hard to degrade, because of the strong bonds in their molecular structure and contribute to a high chemical oxygen demand (COD) and colour (Kreetachat et al., 2007). In addition to these, some toxic compounds such as resin acids, unsaturated fatty acids, diterpene alcohols and others can exist in wastewaters subjected to the process
(Pokhrel and Viraraghavan, 2004). The wastewater generated from this unit is difficult to treat therefore; the wastewater is transferred to chemical recovery unit, so that the chemicals present in the wastewater get recovered and reused.

Effluent generated from bleaching process is generally less polluted as compared to the wastewater discharged from the pulping process, however effluent toxicity is an important issue. If molecular chlorine or chlorine dioxide is used in the bleaching step, chlorinated organic substances such as chloro-phenols, elemental chlorine or chlorine dioxide, calcium oxide, hydrochloric acid, dioxins, resin, fatty acids and furans can be generated. Many of these are very toxic, bio-accumulative, and mutagenic. Inorganic compounds containing chlorate (chlorates) are also formed when chlorine is used in any of its forms in the bleaching process.

The wastewater generated form paper making process contains high concentration of suspended solids (SS), BOD, COD, and inorganic dyes. This increased value is because during the process pigments, binder and fibres got leached into the effluent (Pokhrel and Viraraghavan, 2004; Fontanier et al., 2006).

Due to the severe toxic effects of pulp and paper mill effluent, there is an urgent need to reduce pollution load before it is discharged into the environment. For efficient treatment technologies, it is important to assess the actual load of pollution, in terms of selected wastewater parameters, exerted by each individual processing unit of mills (Kansal et al., 2008). Considering the need to characterize the physicochemical properties of pulp and paper mill effluent, the present chapter was undertaken with the objective to portray the physico-chemical parameters of each unit of pulp and paper industry. The data would be useful in developing innovative effluent treatment techniques for pulp and paper industry.

3.2. Material and Methods

3.2.1. Equipments, Glass wares, Plastic wares and Miscellaneous

(i) Equipments

The equipment used during the present study includes laminar flow (Kartos International), pH meter (Lab India), Magnetic stirrer (Matrix), Centrifuge (Sorvall –
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RC 5B Plus), Spectrophotometer (Pharmaspec UV - 1700, Shimadzu), Pipettes (Eppendorf), COD analysis apparatus (Reflux condenser tube method, Spectralab), BOD Incubator (Caltan), Analytical balance (Sartorius), Drying oven (Metrix), Vacuum pump (Thomas), Filtration apparatus (Tarsons), Electronic Burette (Eppendorf), and Thermometer (Hicks).

(ii) Glassware/Plastic Ware

Storage bottles, Wash bottles, and tips etc., were of Tarsons make. Measuring cylinders, conical flasks, beakers, erlenmeyer flasks, Durham, bottle, test tube, petridish were procured from M/s. Borosil. All glassware and plastic ware were cleaned by washing with mild detergent followed by rinsing with tap water and finally with distilled (water DW).

(iii) Miscellaneous

Tongs and insulated gloves, Glass fiber filters, Forceps, Porcelain evaporating dishes with 100 ml capacity Aluminum weighing dish and filter were procured from Abdos

3.2.2. Reagents

- **Standard pH Buffer Solution**: standard buffer solution of pH 4.0, 7.0 and 9.2 was prepared by dissolving buffer tablets (Fisher Scientific) in DW and stored at 4.0°C.
- **Hydrochloric Acid (HCl) 10%**: 31.3 ml of 32% concentrated HCl was added in 68.7 ml of DW. The solution was mixed properly and kept at room temperature for future use.
- **Sodium Hydroxide (NaOH) 10%**: 10 g of sodium hydroxide was dissolved in 80 ml of DW and the final volume was made up to 100 ml. The solution was mixed properly and kept at room temperature for future use.
- **Acetic Acid (10%)**: an amount of 100 ml reagent grade acetic acid was poured in to 1000 ml DW.
- **Sodium Nitrite (10%)**: an amount of 0.02g of sodium nitrite was dissolved in 100ml DW If the solution contains any suspended particles or sediment, filter through a coarse sintered glass filter. The clear solution is stored in a glass stopper bottle.
- **Ammonium Hydroxide (2N):** an amount of 135 ml concentrated ammonium hydroxide was poured into 1000 ml DW. This solution was stored in a borosilicate glass bottle and was used only as long as it remains free from sediment when mixed with the sample of dissolved lignin in the procedure used to test reagent purity.

- **Potassium Chloroplatinate Standard:** dissolved 1.246 gm of potassium chloroplatinate ($K_2PtCl_6$) equivalent to 500 mg metallic platinum and 100 mg crystallized cobaltous chloride ($CoCl_2.6H_2O$) equivalent to 250 mg metallic cobalt with 100 ml concentrated HCl and diluted it to 1000 ml with distilled water. This stock standard has a colour of 500 units.

- **Potassium Dichromate Solution ($K_2Cr_2O_7$) (0.25 N)** - $K_2Cr_2O_7$, dried at 103°C for 2 hrs allowed to cool down in desiccators. Accurately weighed 6.1295 g of $K_2Cr_2O_7$ was added in 500 ml distilled water followed by the addition of 0.06 g of sulphanic acid.

- **Ferrous Ammonium Sulphate (FAS) (0.1 N)** – accurately weighed 39 g of FAS was dissolved in 500 ml distilled water followed by the addition of 20 ml of $H_2SO_4$. Finally, the volume was made up to 1000 ml with distilled water.

- **Sulphuric Acid Reagent ($H_2SO_4$)** - accurately weighed 10 g of silver sulphate ($Ag_2SO_4$) was dissolved in 1 L of $H_2SO_4$ and left overnight to dissolve.

- **Ferroin Indicator** - an amount of 1.485 g of phenanthroline monohydrate and 0.6959 g of silver sulphate hepta hydrate ($FeSO_4.7H_2O$) was dissolved in 100 ml distilled water.

- **Dilution Water Reagents**
  - **Phosphate Buffer Solution** (pH 7.0, 0.05 M), was prepared by using these chemicals:
    - $KH_2PO_4$ 8.5 g
    - $K_2HPO_4$ 21.7 g
    - $Na_2HPO_4.7H_2O$ 33.4 g

    All the above constituents were dissolved in the 600 ml of distilled water and then the pH was adjusted to 7.0. Then, 1.7 g of $NH_4Cl$ was added and finally the volume was made up to 1 L.
- **Magnesium Sulphate Solution**: 22.5 g of MgSO$_4$ was dissolved in 1 L of distilled water.
- **Calcium Chloride Solution**: 27.5 g of CaCl$_2$ was dissolved in 1 L distilled water.
- **Ferric Chloride Solution**: 0.25 g of FeCl$_3$.6H$_2$O was dissolved in 1 L distilled water.
- **Alkaline Iodide Azide Solution**
  Following chemicals were dissolved in 500 ml of distilled water.
  
  \[
  \begin{array}{ll}
    \text{NaOH} & 250 \text{ g} \\
    \text{NaI} & 67.5 \text{ g} \\
    \text{NaN}_3 & 5.0 \text{ g}
  \end{array}
  \]
- **Manganese Sulphate**: 91.06 g MnSO$_4$.7H$_2$O was dissolved in 250 ml of distilled water.
- **Sodium Thiosulphate Solution (Hypo) 0.125 N**: 3.102 g Na$_2$S$_2$O$_3$.5H$_2$O was weighed and dissolved in 60 ml of distilled water. Finally volume was made 100ml with distilled water. The working solution (0.125 N) was made fresh prior to each analysis.
- **Potassium Iodate (0.0125 N)**: 0.466 g KIO$_3$ was dissolved per liter of distilled water
- **Potassium Iodide (0.5 g)** added directly while the standardization of sodium thiosulphate is being carried out.
- **Starch Indicator Solution (2%)**: 2 g of starch was dissolved in 100 ml of hot distilled water.

3.2.3. Mill Description

The mill used in the present study is an old mill, almost half a century old and was installed with capacity of 200 tons of pulp production per day. It produces various types of writing and printing paper (book printing, map printing, magazine printing photocopy paper wedding invitation etc.), business communication paper (computer stationary colour decorative paper envelope identity card) and other like soap wrapper cigarette wrapper etc. It is a large-scale paper mill situated in Western Uttar Pradesh.
India. This mill use hardwood (bamboo and eucalyptus), and wastepaper, as raw materials. The pulp is generated from the raw material through Kraft pulping. Following pulping, the pulp is bleached through various chemicals, but this step is preceded by oxygen delignification of the pulp. The chemical bleaching is completed in four stages, viz., Chlorine Dioxide treatment, Caustic Extraction, Hypochlorite treatments in two stages (CEHH). Each step is preceded and followed by counter-current washing with fresh water. A total of 25,000 KLD (kiloliter per day) of water is consumed during pulping and paper making processes, from which around 22,000 KLD of water is discharged as wastewater.

3.2.4. Treatment Process

3.2.4.1. Chemical Recovery

Chemical recovery process is performed in three steps

Step 1 - Evaporation: Evaporation is carried out using multiple effects, normally 5 to 7 effects in series. In systems of this type, the vapor obtained in one evaporator effect becomes the heating steam for the next effect. Process steam enters the system at effect no. 1, while the vapor from the last effect is condensed, producing a vacuum in the latter effects.

Step 2 - Combustion: Combustion of the black liquor in the recovery boiler to compensate for chemicals that are being lost in the pulp mill cycle, sodium and sulphur chemicals are added to the black liquor before combustion. The recovery boiler burns the organic material in the concentrated black liquor, at the same time reducing the oxidized sulphur compounds to sulphide.

Step 3 - Causticizing: Causticizing plays an important role in the chemical balance of a kraft mill, as this process generates cooking liquor The object of the causticizing process is to turn inactive sodium carbonate (Na$_2$CO$_3$) into the active cooking chemical, sodium hydroxide, and to make sure that the conversion efficiency of carbonate into hydroxide is as high as possible.
3.2.4.2. Existing Effluent Treatment Plant

Waste water generated from all the processes were collected and discharged to effluent treatment plant for its physical, chemical and biological treatment. A flow sheet of effluent treatment plant is given in figure 3.1. Brief description of existing effluent treatment plant is as follows:

(i) Primary Clarifier

The purpose of primary clarifier is to remove the suspended solids. Normally 65-75% suspended solids and 20-30 % BOD are removed by primary clarification. Wastewater containing fibers from the pulp lines is pumped to primary clarifier (sedimentation tank) where it was cooled down and settled before biological treatment. The settled fiber-sludge is taken out from the sedimentation basins and led to a fiber recovery system, and the clarified wastewater is led to aeration tank entering the biological treatment. Primary clarifier is circular with a Surface Overflow Rate (SOR) of 16-20 m³/m²/day having retention time of 5-6 hrs. The depth of the side wall is 5.49 m, diameter is 48.77 m and it has capacity of 10088 m³.

(ii) Aeration Tank

Aeration tank is used for secondary treatment. The purpose of secondary treatment is to remove the soluble organics and to further remove suspended solids. These removals are achieved by using biological treatment process in aeration tank. Allowing microorganisms to utilize the pollutants as nutrients where dissolved organic compounds and colloidal particles can be lowered and oxidized into low molecular fractions. The microorganisms grow and multiply in an aerobic environment, forming a sludge which is later separated (Persson, 2011). Aeration tank is rectangular in shape with length of 104 m, width 40 m, depth 4.5m and total capacity of 18720 m³. It has a retention time is 18 hrs and 12 surface aerators of 50 Hp are used for the process of aeration.
(iii) Secondary Clarifier

The purpose of secondary clarification is to remove the settleble biomass. The design objective of a secondary clarifier is to provide sufficient time for maximum settling of active biomass generated in aeration tank. The overflow of the Secondary Clarifier is the final discharge. Retention time is 4 hrs. Dimension of secondary clarifier is: diameter 45.72 m, side wall depth 3.66m and total capacity 6005 m$^3$.

3.2.4.3. Recycling of Waste Water

With the ease of water availability at practically free of cost, the major trend in the mills till recent past was to use fresh water in its all operations resulting in high water consumption and accordingly high volume of waste water being discharged. With increasing emphasis on conservation of natural resources and also to achieve cost effective production, the mills have realized the need for practicing the recycle concept in the area of basic utilities such as water, fibers, chemicals and energy.

The concept of recycling water is to save this natural resource. In pulp and paper sector, the wastewater from the units like paper machine and bleaching unit are recycled to some extent.

![Flow sheet of effluent treatment plant](image)

**Figure 3.1:** Flow sheet of effluent treatment plant
3.2.5. Sampling

It is an old axiom that the result of any testing method can be no better than the sample on which it is performed. The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purpose while still accurately representing the material being sampled. This objective implies that the relative proportions or concentrations of all pertinent components will be the same in the sample as in the material being sampled, and that the sample is handled in such a way that no significant changes in composition occur before the tests are made.

There are two main types of samples which are used in water and wastewater treatment: grab samples and composite samples. The type of sample taken in a given instance will depend on the type of test to be performed, the frequency of testing, and on permit requirements.

3.2.5.1. Grab Sample

A grab sample, also known as a catch sample, consists of a single sample taken at a specific time. This is the most common type of sample and is the sampling technique used. A grab sample has certain limitations. In essence, a grab sample takes a snapshot of the characteristics of the water at a specific point and time, so it may not be completely represent the entire flow. Grab samples are most appropriate to small plants with low flows. On the other hand, grab samples do provide an immediate sample, and are thus to be preferred for some tests. Specifically, pH, dissolved oxygen, and total residual chlorine can change very rapidly in water once the sample is removed from the flow, so grab samples are preferred for these tests. Grab samples must be collected carefully to make them as representative as possible of the water as a whole. They should be taken at a time of day when the plant is operating near its average daily flow rate (figure 3.2).
3.2.5.2. Composite Sample

A composite sample, also known as an integrated sample, is a sample which consists of a mixture of several individual grab samples collected at regular and specified time periods, each sample taken in proportion to the amount of flow at that time. Composite samples give a more representative sample of the characteristics of water at the plant over a longer period of time. Like grab samples, composite samples have both strengths and weaknesses and are not acceptable for all tests. The greatest strength of composite samples is their ability to take into account changes in flow and other characteristics of the water over time. This helps to gain an overall picture of the total effects that the influent will have on the treatment process and that the effluent will have on the receiving water. However, composite samples cannot be used for tests of water characteristics which change during storage (such as dissolved oxygen) or of water characteristics which change when samples are mixed together.

3.2.5.3. Sample Containers

Clean plastic containers made of fluorinated polymers such as poly-tetra-fluoro-ethylene (PTEF), free of contaminants were used for sampling. Containers were rinsed with effluent before filling it.

3.2.5.4. Sample Collection

For the present study, samples were collected from various processing units of mills. The major sampling sources were from the bleach plant waste (chlorination stage,
extraction stage, hypochlorite stage and combined bleach plant), primary clarifier inlet (combined effluent from whole process of mill) primary clarifier outlet (PC outlet) and secondary clarifier outlet (SC outlet). SC outlet is finally mill treated effluent. To have true and representative samples, 24 hrs composite sampling was carried out. Samples were collected from aeration tank of mill ETP, for the analysis of MLSS, SVI and DO. Samples were collected in clean containers and were transported to lab within 4 h under cool condition.

3.2.5.5. Sample Preservation

Complete preservation of samples, either domestic sewage, industrial wastes or natural waters, is practically impossible. Regardless of the sample, complete stability for every constituent can never be achieved. At best, preservation technique can only retard the chemical and biological changes that take place in a sample after the sample is removed from the parent source. To maintain the integrity of the sample, appropriate selection of container, pre-treatment of container is necessary. To minimize the potential for volatilization or biodegradation between sampling and analysis, the samples were kept at cool place without freezing. Therefore, the collected composite samples were kept at refrigeration system set at 4°C.

3.2.6. Characterization of Effluent

Effluents from pulp and paper industries are often very complex, and it is almost impossible to characterize all types of constituents. Effluent generally contains carbohydrates (cellulose glucose, xylose, galactose, manose, arabinose etc.), extractives (fatty acids, resin acids, triglycerides), chlorolignin and low molecular weight compounds (formic acid, acetic acid, oxalic acid) (Catalkaya and Kargi, 2008). Samples were analyzed for major physicochemical parameters, viz. pH, colour, lignin content, chemical oxygen demand (COD), biochemical oxygen demand (BOD). The profile of solids present in different forms, viz. total solids (TS), total suspended solids (TSS) and total dissolved solids (TDS) was also studied. The experiments were carried out in triplicates in order to access the repeatability of the results. All the analyses were carried out as per standard procedure (APHA, 1998). The pH of the effluent samples was analyzed using microprocessor pH meter and colour was measured by spectrophotometric method.
3.2.6.1. Estimation of Temperature

A temperature is a numerical measure of hot and cold in a body that is in its own state of internal thermal equilibrium. Its measurement is done by detection of heat radiation or particle velocity or kinetic energy, or by the bulk behavior of a thermometric material. It may be calibrated in any of various temperature scales: Celsius, Fahrenheit, Kelvin, etc. Different units (chlorination, extraction, hypochlorite, combine bleach plant, PC outlet, PC inlet and SC outlet) of pulp and paper wastewater have different temperatures. Temperature was measured by using calibrated thermometer.

3.2.6.2. Estimation of pH of the Effluent

(i) Scope

This method describes the procedures for determining the pH of effluent, to indicate presence of either acidic or basic ions which contribute towards physic-chemical properties of the effluent.

(ii) Method

pH meter was calibrated by using standard pH buffer solution (pH 4.0, 7.0 and 9.2). The effluent (50 ml) was poured in 100 ml of beaker. A 100 ml of glass beaker with 50 ml of effluent and a magnet bead was placed on a magnetic stirrer. The electrode of a pH meter was dipped into the sample and pH was monitored under stirring conditions till the pH became constant.

3.2.6.3. Estimation of Lignin Content

(i) Scope

Lignin is a natural plastic containing carbon, hydrogen and oxygen composed of phenylpropane units, lignin is heterogeneous and chemically complex. It is synthesized by higher plants, reaching levels of 20-30% of the dry weight of woody tissue, next to cellulose; it is the second most abundant compound in plant biomass. In nature it is very resistant to degradation, being held together with strong chemical bonds. Lignin is actually not single compound but it is the combination of several units which are covalently bonded. All are complex, amorphous, three dimensional
polymers that have in common a phenylpropane structure, that is, a benzene ring with a tail of three carbons. In their natural unprocessed form, they are so complex that none of them has ever been completely described, and they have molecular weights that may reach 15,000 or more. In the pulp and paper manufacturing process it is removed by using chemicals and it is the main constituent responsible for color in pulp and paper industry effluent. The estimation of lignin was done by using modified Perl and Benson (Nitrosation) method (Lin and Dence 1992).

(ii) Method

The effluent sample was allowed to stand for 12 hr to 24 hr at room temperature after which the clear supernatant was decanted off. A 50 ml sample of wastewater was placed in a 125 ml glass stopper Erlenmeyer flask and 1ml each of the acetic acid and sodium nitrite solutions was added with the help of a pipette. The solution was mixed by swirling and allowed to stand for 15 min at room temperature. Two ml of the ammonium hydroxide solution was added from and mixed; the solution was allowed to stand for 10 min at room temperature. The absorbance \( A_T \) was recorded at 430 nm in a cell with a 1.0 cm light path against a distilled water reference. The blank absorbance \( A_b \) was determined in the same way except that the reagents are added to the water sample in order: acetic acid, ammonium hydroxide, sodium nitrite. Colored nitro compounds are not formed in the basic solution and thus the blank absorbance was due to the reagents and the substance originally present in the water.

(iii) Calculation

The net absorbance is calculated as the difference between \( A_T \) and \( A_b \). Lignin concentration is calculated from the Beer-Lambert equation

\[
C = \frac{A_s}{ab}
\]

Where

\[
\begin{align*}
\text{a} & = \text{absorptivity, cm}^{-1} \text{ ppm}^{-1}, \\
\text{As} & = \text{net absorbance}, \\
\text{C} & = \text{concentration of lignin (10% solids basis), ppm}, \\
\text{b} & = \text{length of light path, cm}
\end{align*}
\]
3.2.6.4. Estimation of Colour

(i) Scope
The standard method for measuring colour is Platinum-Cobalt method. In the wastewater samples colour is due to naturally occurring materials like lignin. At different pH, the colour intensity of solutions was different.

(ii) Method
The intensity of colour was measured in accordance with the Canadian Pulp and Paper Association Standard Method. The samples were centrifuged at 10,000 rpm for 10 min to remove suspended solids. The pH of the supernatant was then adjusted to 7.0-7.5, and thereafter the absorbance was measured at 465 nm using distilled water as blank.

(iii) Calculation
The absorbance values were transformed into colour units (PCU) as follows:

\[
\text{Colour (PCU)} = 500 \times \frac{A_2}{A_1}
\]

Where
\[A_1 = \text{absorbance of 500 PCU of standard platinum – cobalt solution (0.1214)}\]
\[A_2 = \text{absorbance of the effluent samples}\]

3.2.6.5. Estimation of Chemical Oxygen Demand (COD)

(i) Scope
The COD is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to the oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring, after correlation has been established. The method involves oxidation of organic matter with boiling mixture of chromic and sulphuric acid. A sample is refluxed in strong acid solution with a known volume of potassium dichromate \((\text{K}_2\text{Cr}_2\text{O}_7)\). After 2 hrs digestion at 150°C, the remaining unreduced dichromate is titrated with ferrous ammonium sulphate to determine the
amount of dichromate consumed and the oxidizable organic matter is calculated in terms of oxygen demand.

(ii) Methods

COD was estimated by using standard method (APHA, 1998). Pre-dried COD tubes were placed in the COD digestion chamber and then accurately measured 0.4 g of HgSO₄ was added to each tube followed by the addition of 20 ml of sample. After that 10 ml K₂Cr₂O₇ solution and 30 ml of H₂SO₄ was added in each tube. The tubes were connected to the condenser and refluxed at 150°C for 2 hrs. After 2 hrs of incubation, the tubes were allowed to cool down to 35-40°C, and then, 80 ml of distilled water was added to rinse the condenser. The contents of the tubes were emptied in separate erlenmeyer flasks. Approximately 4-5 drops of ferroin indicator was added in each of the digested samples prior to titration. The digested samples were titrated against 0.1 N FAS (ferrous ammonium sulphate), which was standardized before every titration. The end point of the titration was denoted as green to wine red colour of solution. Standardization of ferrous ammonium sulphate is necessary. For this 90 ml distilled water, 10 ml of K₂Cr₂O₇ was added followed by the addition of the 30 ml conc. H₂SO₄. This reaction mixture was allowed to cool down to room temperature and titrated against FAS using ferroin as an indicator. End point green to wine red was observed.

(iii) Calculations

\[
COD (mg/ l) = (A-B) * N_{FAS} * 8000 / ml of sample
\]

Where

A = ml of the FAS used for the blank
B = ml of the FAS used for the sample
N_{FAS} = Normality of the FAS

3.2.6. Estimation of Biochemical Oxygen Demand

(i) Scope

Biochemical oxygen demand or BOD is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present
in a given water sample at certain temperature over a specific time period. The term also refers to a chemical procedure for determining this amount. This is widely used as an indication of the organic quality of water. The BOD value is most commonly expressed in milligrams of oxygen consumed per litre (L) of sample during 5/3 days of incubation at 20/27 °C and is often used as a robust surrogate of the degree of organic pollution of water.

(ii) Method

Preparation of dilution water: standard method (APHA) was used for BOD estimation of effluent, for this, distilled water (DW) was aerated for 20-25 hrs. After that MgSO$_4$, CaCl$_2$, FeCl$_3$, seeding material (sewage) (0.1% each) were added. The distilled water cane was shacked in order to mix all the elements present in the dilution water.

Samples were appropriately diluted depending on their COD values, using dilution water and then BOD bottles were rinsed with appropriate samples and filled up to the brim. The bottles to be used for the estimation of dissolved oxygen for zero day were kept aside, while the rest of the bottles were incubated at 27°C for 3 days in dark in a BOD incubator.

Determination of initial DO: fixation of the BOD bottles was done by adding 2.0 ml of MnSO$_4$ followed by 2.0 ml of alkali azide. Bottles were shaken and precipitates were allowed to settle down for 20 to 30 min. Then, 2.0 ml of H$_2$SO$_4$ was added. Bottles were shaken properly for no particulate matter. 100 ml of this reaction mixture was transferred to erlenmeyer flask and titrated against the freshly prepared 0.0125 N Hypo solution using starch as an indicator. For the determination of the DO of the BOD bottles, which were incubated for 3 days for 27°C the above mentioned step was repeated.

Standardization of hypo: KIO$_3$ 10 ml and 90 ml of DW was added followed by H$_2$SO$_4$. This was immediately titrated against 0.0125 N hypo solution after the addition of 0.5 g KI using starch as an indicator. End point to be observed was blue to colorless.
(iii) Calculation

\[
\text{BOD mg/L} = (D_1-D_3)-(B_1-B_3)/\% \text{ of sample used}
\]

Where

\[D_1 = \text{DO of the dilute sample immediately after preparation (mg/L)}\]
\[D_3 = \text{DO of diluted sample after the incubation for 3 days (mg/L)}\]
\[B_1 = \text{DO of the blank immediately after preparation (mg/L)}\]
\[B_3 = \text{DO of blank after incubation for 3 days.}\]

3.2.6.7. Estimation of Total Solids (TS)

(i) Scope

Solids refer to matter suspended or dissolved in water or wastewater. These affect water or effluent quality in a number of ways. Water with high dissolved solids may induce unfavorable physiological reaction to the transient consumer. Total solids are the term applied to the material residue left in a vessel after evaporation of a sample and its subsequent drying in an oven. Total solids include total suspended solids (TSS) and total dissolved solids (TDS).

(ii) Method

The glass beakers were washed with distilled water labeled by using tape and permanent marker, and placed in oven at 103 ± 2°C for one hour. After that removed from oven and placed in desiccators to cool. When cooled, weighed to the nearest 0.0001 g (= 0.1 mg) till the constant value and recorded the weight as "beaker pre-weight" in lab notebook. Stored upside-down in a clean, dried, covered container until ready to use. Shaken sample bottle vigorously to suspend any sediment that has settled on the bottom. Poured 100 ml sample into the beaker and placed beakers with effluent sample in an 80°C oven and kept until all the liquid has evaporated. Once the water had been removed, increased oven temperature to 103 ± 2°C for at least two hours. Placed beakers in desiccator to cool before weighing. Weighed to nearest 0.0001 g (0.1 mg) and record as "beaker post-weight."
(iii) Calculations

TS (mg/l) = (Beaker Post-Weight (mg) - Beaker Pre-Weight (mg) × 1000/ Sample vol. (ml)

3.2.6.8. Estimation of Total Suspended Solids (TSS)

(i) Scope

The residue obtained after a thoroughly mixed sample is filtered and dried at 103 ±2°C represents the amount of solids suspended in the sample solution. The amount of suspended solids in a water sample may be used as a general indicator of the overall quality of the sample. Suspended solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with discharge regulations.

(ii) Method

Each filter was washed with distilled water and placed into a weighing dish. All filters were kept into the preheated oven for 1 hr. After that all filters were placed into the desiccators and cooled for 15 min. checked calibration of analytical balance and each filter paper was weighed till the constant value on analytical balance was recorded. Clean dry filter was placed on the filter funnel and filtered the 100 ml mixed sample with the help of vacuum pump. The graduated cylinder was rinsed thoroughly with distilled water poured into funnel to wash any material adhering to the sides of funnel onto the filter with distilled water. Filter was transferred to the weighing dish. All filters were placed into oven and dried filters for 1 hr. in the oven. After that filters were placed in desiccators for 15 min. Filters were weighed on analytical balance and recorded dry weight.

(iii) Calculations

Total suspended solids (mg/l) = (A-B) x 1000/Sample volume (ml)

Where

A = Weight of filter+ dried residue (mg)
B = Weight of filter (mg)
3.2.6.9. Estimation of Total Dissolved Solids (TDS)

(i) Scope

If a well mixed sample filtered through a prepared glass fiber filter into a clean filter flask. The portion of the sample that was not retained by the filter was the dissolved solids. Total dissolved solids (TDS) comprise inorganic salts and small amounts of organic matter that are dissolved in water. The principal constituents are usually the cations calcium, magnesium, sodium and potassium and the anions carbonate, bicarbonate, chloride, sulphate and, nitrate.

(ii) Method

For estimation of TDS, glass beakers were washed with distilled water and labeled them using permanent marker. The glass wares were kept in oven at 103 ± 2°C for one hr. After 1 hr the beakers were removed from oven and placed in desiccators to cool. When cooled, weighed to the nearest 0.0001 g (= 0.1 mg) till the constant value and weight was recorded as "beaker pre-weight" in lab notebook. Stored upside-down in a clean, dried, covered container until ready to use. Each filter was washed with distilled water and placed into a weighing dish. All filters were placed into the preheated oven for 1 hr. After 1 hr, all filters were placed into the desiccators and cooled for 15 min. A clean dry filter was placed on the filter funnel and filtered well mixed sample (150 ml) with the help of vacuum pump. Beakers were placed containing filtered effluent sample at 80°C in an oven, kept until all the liquid has evaporated. Once the water has been removed, oven temperature was increased to 105°C for at least two hours. After two hrs beakers were placed in desiccators, to cool before weighing and weighted to nearest 0.0001g (0.1 mg) and record as "beaker post-weight."

(iii) Calculations

\[
\text{TDS (mg/l)} = (\text{Beaker Post-Weight (mg)} - \text{Beaker Pre-Weight (mg)} \times 1000/ \text{Sample vol. (ml)}
\]
3.3. Results

3.3.1. Temperature

The measurement of temperature is important because most wastewater treatment schemes include biological processes that are temperature dependent. The temperature of wastewater varies from season to season and also with geographic location. The results for different streams revealed that the temperature of each unit was different. Table 3.1 shows the range of temperature measured during summer and winter.

Table 3.1: Temperature range of effluent emanated from different units

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Different Unit</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chlorination</td>
<td>45ºC - 55ºC</td>
</tr>
<tr>
<td>2</td>
<td>Extraction</td>
<td>50ºC - 60ºC</td>
</tr>
<tr>
<td>3</td>
<td>Hypochlorite</td>
<td>50ºC - 60ºC</td>
</tr>
<tr>
<td>4</td>
<td>Combine Bleach Plant</td>
<td>40ºC - 50ºC</td>
</tr>
<tr>
<td>5</td>
<td>PC Inlet</td>
<td>25ºC - 38ºC</td>
</tr>
<tr>
<td>6</td>
<td>PC Outlet</td>
<td>20ºC - 35ºC</td>
</tr>
<tr>
<td>7</td>
<td>SC Outlet</td>
<td>18ºC - 32ºC</td>
</tr>
</tbody>
</table>

3.3.2. pH

As a chemical component of the wastewater, pH has direct influence on wastewater treatability regardless of whether treatment is physical/chemical or biological. Because it is a critical component of the wastewater, it is therefore critically important to treatment.

The pH of the environment has a profound effect on the rate of microbial growth by affecting the functionality of metabolic enzymes. Acidic conditions (low pH) or basic conditions (high pH) alter the structure of the enzyme and stop growth. Most of the microorganisms do well within a pH range of 6.5 to 8.5. However, some enzyme systems can tolerate extreme pH and will thrive in acidic or basic environments. Abnormal or irregular pH in biological treatment processes can result in a significant decrease in the rate of removal of organic compounds from the effluent, which will affect the effluent properties.
The pH was analyzed by collecting the samples from different units. Six samples were collected at different time intervals, two samples in June-July, two in Sept-Oct, and finally two samples in the month of January-February. The units selected were chlorination, extraction, hypochlorite treatment, combined bleach plant, PC inlet, PC outlet and SC outlet. The pH of waste water from chlorination unit showed values ranging from 2.4-3. The standard deviation between the collected samples was 0.21. While observing the extraction unit the values ranging from 8.5-10.5 with a standard deviation among the values of 0.65. Whereas in case of samples collected from hypochlorite treatment, the range was in between 4 - 6 with a standard deviation of 0.67. After this the samples from combined bleach effluent was analyzed for the same parameter i.e., pH and it was observed that the values ranging from 5 - 7.5 with the standard deviation of 0.83. Finally the samples from PC inlet, PC outlet and SC outlet were analyzed and the values were ranging from 8.5 - 10, 6.5 - 8, and 6.8 - 8 respectively. The standard deviation between the samples collected from these units was 0.49, 0.48 and 0.38 respectively (Table 3.2).

Table 3.2: pH of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td>2.4</td>
<td>2.8</td>
<td>2.5</td>
<td>3</td>
<td>2.5</td>
<td>2.6</td>
<td>2.63</td>
<td>0.21</td>
</tr>
<tr>
<td>Extraction</td>
<td>9.5</td>
<td>9.5</td>
<td>10</td>
<td>8.5</td>
<td>9</td>
<td>10.5</td>
<td>9.5</td>
<td>0.65</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>4.5</td>
<td>5</td>
<td>5.5</td>
<td>4</td>
<td>4.5</td>
<td>6</td>
<td>4.92</td>
<td>0.67</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>6.5</td>
<td>5</td>
<td>6</td>
<td>7.5</td>
<td>5.5</td>
<td>6.8</td>
<td>6.16</td>
<td>0.83</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>9.3</td>
<td>8.5</td>
<td>8.8</td>
<td>10</td>
<td>9</td>
<td>8.7</td>
<td>9.05</td>
<td>0.49</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>7.8</td>
<td>7.5</td>
<td>7.2</td>
<td>8</td>
<td>7.5</td>
<td>6.5</td>
<td>7.34</td>
<td>0.48</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>7.5</td>
<td>8</td>
<td>7.4</td>
<td>7.8</td>
<td>6.8</td>
<td>7.4</td>
<td>7.48</td>
<td>0.38</td>
</tr>
</tbody>
</table>

3.3.3. Lignin

Pulp and paper mill is a large industrial enterprise that generates significant amount of wastewater containing high concentration of lignin. The results of different units exhibited that quantity of lignin varies in each unit. In chlorination, the lignin, ranged from 95 – 140 mg/l. When estimating the lignin in extraction unit, it was observed that
the lignin ranged from 550 – 720 mg/l. In hypochlorite, it ranged from 225 – 300 mg/l. Units like combine bleach plant, PC inlet, PC outlet and SC outlet lignin varied from 440 – 520 mg/l, 340 – 415 mg/l, 155 – 220 mg/l and 110 – 175 mg/l respectively (Table 3.3).

Table 3.3: Lignin content of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of Lignin (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>120</td>
<td>115</td>
<td>140</td>
</tr>
<tr>
<td>Extraction</td>
<td>720</td>
<td>670</td>
<td>560</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>290</td>
<td>240</td>
<td>300</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>520</td>
<td>490</td>
<td>440</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>410</td>
<td>390</td>
<td>360</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>220</td>
<td>205</td>
<td>190</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>175</td>
<td>165</td>
<td>150</td>
</tr>
</tbody>
</table>

3.3.4. Colour

The colour is usually the first contaminant to be recognized in wastewater/effluent that affects the aesthetics, water transparency and gas solubility of water bodies. The colour of the effluent mainly arises due to the presence of low and high molecular weight chlorinated organic compound generated from the lignin degradation product which are produced during different stages like pulping, and bleaching. Table 3 shows the variation in colour in different sections. Visibly, the effluent had a dark brown to yellowish brown appearance at the time of collection of samples. Colour measures the amount of light that can penetrate the effluent. In certain situation, colour can adversely affect the growth of plants in effluent receiving waters bodies.

Total six samples were collected from each unit in the similar manner as mentioned above in the section 3.3.1. Colour of wastewater from chlorination unit showed values ranging from 530 - 800 PCU. The standard deviation within the samples was 128.80. Deviation was more because the values of the colour varied a lot; this is due to the change in production process and raw material used. Extraction unit showed values ranged from 2100 - 3000 PCU with a standard deviation of 362.25 within the samples.
The results were observed for Hypochlorite unit and it was seen that the values ranged from 470 - 725 PCU with the standard deviation of 84.18 within the samples. Similarly the sample of combine bleach plant was analyzed followed by PC inlet, PC outlet and SC outlet and it was observed that the values ranged from 1750 - 2550 PCU, 1350 - 2100 PCU, 680 - 1060 PCU and 480 - 700 PCU respectively. Standard deviation among the samples for each unit was 307.53, 277.21, 150.48, and 76.59 respectively (Table 3.4).

**Table 3.4:** Colour of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of colour (PCU)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>700</td>
<td>650</td>
<td>800</td>
</tr>
<tr>
<td>Extraction</td>
<td>3000</td>
<td>2700</td>
<td>2300</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>650</td>
<td>590</td>
<td>725</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>2550</td>
<td>1975</td>
<td>1750</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>2100</td>
<td>1540</td>
<td>1400</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>1060</td>
<td>1130</td>
<td>680</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>700</td>
<td>650</td>
<td>560</td>
</tr>
</tbody>
</table>

**3.3.5. Chemical Oxygen Demand (COD)**

Chemical Oxygen Demand is a parameter that represents the amount of oxygen needed for complete decomposition of organic matter. In terms of pulp and paper production, COD originates from dissolved raw materials, process aids and all substances formed during pulp cooking that are not removed with the black liquor. These types of substances are often very persistent and cannot be removed efficiently, causing negative effects on environment.

Different samples were collected for each unit and results were depicted in Table 3.5. The values ranging from 350 - 650 mg/l for chlorination unit with a standard deviation of 95.47 within the samples. While observing the extraction unit the values ranging from 1450 - 1900 mg/l. The calculated standard deviation was 168.42. The results was analyzed for Hypochlorite unit the COD values ranging from 490 - 900 mg/l with the
standard deviation of 145.04. Combine bleach plant showed the values in the range of 1450 - 1950 mg/l and the standard deviation was 193.41 between the samples. Samples from PC inlet showed ranges from 1050 - 1700 mg/l. The calculated standard deviation was 237.02. The COD values for PC outlet and SC outlet was ranging from 580 - 970 mg/l and 240 - 350 mg/l respectively. The standard deviation was 124.75 and 34.69 respectively.

Mean of COD values of different samples were 487.5 mg/l chlorination unit, 1620 mg/l extraction, 699.17 mg/l hypochlorite unit, 1625 mg/l combine bleach plant, 1391.67 mg/l PC inlet, 756 for PC outlet and mean value was 284.17 mg/l of SC outlet.

**Table 3.5:** Chemical oxygen demand of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of COD (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>525</td>
<td>500</td>
<td>650</td>
</tr>
<tr>
<td>Extraction</td>
<td>1900</td>
<td>1700</td>
<td>1450</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>900</td>
<td>775</td>
<td>820</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>1950</td>
<td>1725</td>
<td>1580</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>1500</td>
<td>1100</td>
<td>1050</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>840</td>
<td>970</td>
<td>580</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>350</td>
<td>280</td>
<td>240</td>
</tr>
</tbody>
</table>

**3.3.6. Biochemical Oxygen Demand**

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of waste waters, effluents. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. This test measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron.
The biochemical oxygen demand was analyzed for each unit. In the similar manner as mentioned above the samples were collected the mean values for each unit was 182.5 mg/l for chlorination, 349 mg/l for extraction, 326.67 mg/l for Hypochlorite, 439 mg/l for combine bleach plant, 405 mg/l for PC inlet, 272 mg/l for PC outlet and 21 mg/l for SC outlet. The results of each sample was depicted in table 3.6. For chlorination unit the biochemical oxygen demand values ranging from 150 - 225 mg/l with the standard deviation of 24.11 between the samples. Extraction unit showed the BOD values ranging from 280 - 400 mg/l. The calculated standard deviation was 41.87. BOD for the samples collected from Hypochlorite unit showed values ranging from 270 - 420 mg/l with standard deviation of 59.98. Similarly the parameter was calculated for the samples collected from combine bleach effluent unit and results showed that the values ranging from 350 - 620 mg/l. The calculated standard deviation was 83.17. While observing the results for PC inlet it was found that the value was ranging from 370 - 450 mg/l. The standard deviation for the samples collected was 28.05. Samples were analyzed for PC outlet and SC outlet also. The values of BOD were ranging from 200-310 mg/l and 15 - 28 mg/l respectively. The standard deviation between the samples for these units was 34.85 and 4.24 respectively.

Table 3.6: Biochemical oxygen demand of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of BOD (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>200</td>
<td>170</td>
<td>225</td>
</tr>
<tr>
<td>Extraction</td>
<td>350</td>
<td>310</td>
<td>380</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>420</td>
<td>350</td>
<td>365</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>620</td>
<td>450</td>
<td>420</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>450</td>
<td>425</td>
<td>390</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>200</td>
<td>275</td>
<td>290</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>28</td>
<td>24</td>
<td>18</td>
</tr>
</tbody>
</table>

3.3.7. Total Solids

Total solids are dissolved solids plus suspended and settleable solids in water. Suspended solids include silt and clay particles, plankton, algae, fine organic debris,
and other particulate matter. These are particles that will not pass through a 2-micron filter. The concentration of total dissolved solids affects the water balance in the cells of aquatic organisms.

Total solids in case of pulp and paper are also a problematic issue to be solved. Therefore for each unit the amount of total solids was also estimated. The calculated mean values for each unit was depicted in table 3.7. Total solid value for chlorination units was 1733.33 mg/l, for extraction unit the mean value of six samples collected at different time was 2034 mg/l. Similarly the analysis was made for Hypochlorite, combine bleach effluent, PC inlet, PC outlet and SC outlet unit. For each unit mean value was 2152.2 mg/l, 2236 mg/l, 1950 mg/l, 1260 mg/l and 1115 mg/l respectively. Six samples were collected for each unit results showed that, the values ranging from 1450 - 2000 mg/l in case of chlorination unit with the standard deviation of 181.81. While observing the extraction unit the values ranging from 1375 - 2500 mg/l with the standard deviation of 360.43 between the samples. Samples from hypochlorite unit showed the values ranging from 1790 - 2550 mg/l, standard deviation was 256.87. Similarly the total solids were estimated for combine bleach effluent, PC inlet and PC outlet. The observed values were ranging from 2140 - 2540 mg/l, 1800 - 2150 mg/l and 1050 - 1350 mg/l respectively. The standard deviations for these samples were 134.62 for chlorination unit samples, 147.20 for PC inlet samples and 149.33 for PC outlet samples. The sample from SC outlet was also collected and analyzed for total solids and it was observed that the values ranging from 940 - 1280 mg/l with the standard deviation of 105.63.

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of TS (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>1900</td>
<td>2000</td>
<td>1750</td>
</tr>
<tr>
<td>Extraction</td>
<td>2350</td>
<td>2220</td>
<td>1975</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>2550</td>
<td>2390</td>
<td>2175</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>2540</td>
<td>2170</td>
<td>2350</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>1900</td>
<td>2100</td>
<td>1750</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>1400</td>
<td>1200</td>
<td>1050</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>1280</td>
<td>1130</td>
<td>1080</td>
</tr>
</tbody>
</table>
3.3.8. Total Dissolved Solids

Total dissolved solids are measurement of inorganic salts, organic matter and other dissolved materials in water. In general, TDS is the sum of the cations and anions in water. Ions and ionic compounds making up TDS usually include carbonate, bicarbonate, chloride, fluoride, sulphate, phosphate, nitrate, calcium, magnesium, sodium, and potassium. The values obtained for TDS were more than WHO (World Health Organization) standard of 2000 mg/l for the discharge of wastewater into surface water.

The samples collected from each unit were also analyzed for total dissolve solids. The results were depicted in table 3.8. The values for the samples collected from chlorination unit was ranging from 1360 - 1910 mg/l with standard deviation of 176.23 between the samples. For extraction unit the values ranging from 1130 - 2020 mg/l. The calculated standard deviation was 342.18. Samples from Hypochlorite unit were varied from 1605 - 2290 mg/l with the standard deviation of 255.97. The samples from combine bleach effluent showed values ranging from 1860 - 2290 mg/l. The calculated standard deviation was 138.82. The sample from PC inlet, PC outlet and SC outlet were analyzed for biochemical analyzed and it was observed that the values were ranging from 1360 - 1860 mg/l, 930 - 1370 mg/l and 910 - 1230 mg/l respectively. Standard deviation was 165.81 for PC inlet samples, 143.58 for PC outlet and 102.00 SC outlet.

Table 3.8: Total dissolved solids of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of TDS (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>1790</td>
<td>1910</td>
<td>1630</td>
</tr>
<tr>
<td>Extraction</td>
<td>2020</td>
<td>1970</td>
<td>1645</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>2360</td>
<td>2170</td>
<td>1915</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>2290</td>
<td>1935</td>
<td>2130</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>1550</td>
<td>1690</td>
<td>1360</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>1250</td>
<td>1110</td>
<td>930</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>1230</td>
<td>1090</td>
<td>1040</td>
</tr>
</tbody>
</table>
3.3.9. Total Suspended Solids

Suspended solids are present in sanitary wastewater and many types of industrial wastewater. As levels of TSS increase, a water body begins to lose its ability to support a diversity of aquatic life. Suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases levels of dissolved oxygen in the warmer water holds less oxygen than the cold water.

The total suspended solids were calculated for each unit. The samples from chlorination unit showed the standard deviation of 20.77 with the values ranging from 60 - 125 mg/l. Different units were analyzed for this parameter. The mean value for six samples from each unit was 20.77 (chlorination unit), 45.40 (extraction unit), 24.83 (Hypochlorite unit), 27.98 (combine bleach plant), 75.22 (PC inlet), 25.41 (PC outlet) and 7.31 (SC outlet) respectively. While observing each unit separately it was seen that for extraction unit the values was ranging from 220 - 330 mg/l with the standard deviation of 45.40. For Hypochlorite unit the values ranging from 185 - 260 mg/l with the standard deviation of 24.83. Samples from combine bleach effluent unit showed the values ranging from 190 - 280 mg/l. The calculated standard deviation was 27.98. The values for PC inlet varied from 290 - 530 mg/l with standard deviation of 75.22 between the samples. Samples for PC outlet and SC outlet showed the values ranging from 75 - 150 mg/l and 30 - 50 mg/l respectively. The calculated standard deviation for the samples of these units was 25.41 and 7.31 respectively (Table 3.9).

**Table 3.9**: Total suspended solids of waste water collected from different units of pulp and paper industry

<table>
<thead>
<tr>
<th>Different Units</th>
<th>Estimated values of TSS (mg/l)</th>
<th>Mean</th>
<th>Std Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>Chlorination</td>
<td>110</td>
<td>90</td>
<td>125</td>
</tr>
<tr>
<td>Extraction</td>
<td>330</td>
<td>250</td>
<td>330</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>190</td>
<td>220</td>
<td>260</td>
</tr>
<tr>
<td>Combine Bleach Plant</td>
<td>250</td>
<td>235</td>
<td>220</td>
</tr>
<tr>
<td>PC Inlet</td>
<td>350</td>
<td>410</td>
<td>390</td>
</tr>
<tr>
<td>PC Outlet</td>
<td>150</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>SC Outlet</td>
<td>50</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>
After seeing all the results it can be concluded that no two units can have same wastewater characteristics. Due to the diversity in usage of raw materials, scale of production and effluent treatment strategies, there is a wide variation in the characteristics of the discharges (Thompson et al., 2001).

3.4. Discussion

Variations in temperature affect all biological processes. There are three temperature regimes: the mesophilic over a temperature range of 4 to 39°C (39.2 to 102.2°F), the thermophilic which peaks at a temperature of 55°C (131°F), and the psychrophilic which operates at temperatures below 4°C (39.2°F). For economic and geographical reasons, most aerobic biological treatment processes operate in the mesophilic range, which is shown in figure 3.3. In the mesophilic range, the rate of the biological reaction will increase with temperature to a maximum value at 31°C (87.8°F) for most aerobic waste systems. A temperature above 39°C will result in a decreased rate for mesophilic organisms. At temperatures above 35.5°C there is deterioration in the biological floc. Protozoa have been observed to disappear at 40°C (104°F) and a dispersed floc with filaments to dominate at 43.3°C (110°F) (Eckenfelder, 2000).

![Figure 3.3: Effect of temperature on biological oxidation](source)

Metcalf and Eddy in 2004 mentioned that the optimum temperatures for bacterial activity are in the range from 25 to 35°C (77 to 95°F). The aerobic digestion and nitrification stops when the temperature rises to 50°C (122°F). When the temperature drops to about 15°C (59°F), methane-producing bacteria become quite inactive, and at about 5°C (41°F), autotrophic-nitrifying bacteria practically cease functionality. At 2°C (35.6°F), chemo-heterotrophic bacteria acting on carbonaceous material become essentially dormant. Another researcher Grady et al. (1999) reported that temperature affects the performance of activated sludge systems as a result of its impact on the rates of biological reactions. The maximum acceptable operating temperature for typical activated sludge systems is limited to about 35° to 40°C (95 to 104°F), which corresponds to the maximum temperature for the growth of mesophilic organisms. Therefore, the unit selected for the study based on the temperature was PC outlet where temperature ranged between 20 - 35°C.

Pollution load of the pulp and paper mill effluents depends significantly upon the nature and cleanliness of the feed stock; whether the pulp and paper mill is equipped with a chemical recovery plant, the bleaching sequence employed and the efficiency of white water recycle in the paper line. The pH of wastewater samples is very important to be monitored as it determines the feasibility of a particular sample to be biologically treated (Jivendra, 1993; Pepper et al., 1996). Biological treatment can be suitably applied to wastewater only if pH values are near neutral. Acidic and basic character of the wastewater has negative effect on the microorganisms and thus leads to inefficient treatment (Atlas, 1993).

Colour of effluent in every unit varied. It was evident from the data that all the units of paper mills produce colored effluent but the quantity might be different. The digester house liquor or the black liquor is dense-brown in colour as it contains majority of unused chemicals and lignin that has been separated during pulping (Bajpai et al., 1993). The spent liquor generally contains sodium lignates mixed with sodium thiolignates along with other chemicals including residual cooking chemicals (Sjostrom and Allen, 1994). The high colours of bleaching wastes are attributable to the extensive usage of bleaching chemicals like chlorine to obtain white pulp (Talka, 1983). Such
Chemicals quench out most of the colored components of the digested pulp, including lignin and other phenolic chromophores. Although the high molecular weight (HMW) fraction of the bleachery effluent is generally believed to be derived from Kraft lignin extracted from the pulp during the chlorination (C) and caustic extraction (E) (Konduru et al., 2001), there is some evidence that colour may also be derived from pulp carbohydrates (Ziobro, 1990). Sankaran and Ludwig (1971), have reported that the double bond conjugated with aromatic ring, quinone methides, and quinone groups are responsible for the colour of its solution. Colour levels of these units were variable which could be due to the differences in the type and quality of process involved and chemical utilized during the process by each mill.

The pulping process plays a central role in the pollution load and composition of the wastewater produced by the pulp and paper mills (Ali and Sreekrishnan, 2001). Digester house liquors contain high amounts of chemicals, lignin, residual fibers, etc., which result in increased levels of COD and BOD in such discharges. The TDS levels are indicative of the presence of high levels of both inorganic and organic compounds present in a given water sample. The Total Dissolved Solids were also alarmingly high in pulp and paper mill wastewater, crossing the limit set by the regulatory authorities. The TDS is also one of the often-neglected parameters, even though it can have tremendous effects on the overall quality of water. Highly significant differences were thus found between all the processing units of pulp and paper mill. It is apparent that no two units may discharge identical effluents since they may adopt any combination(s) of the number of technologies and chemicals for in the process involved in the manufacturing of pulp and paper (Ali and Sreekrishnan, 2001).

Chlorination in the pre-bleach cycle begins with washed brown stock pulp slurry at low consistency (3 to 5 percent weight of pulp to water) being pumped into a chlorination mixer. Chlorine gas, which is often dispersed in water, is added to the pulp slurry in the mixer and is vigorously mixed. The reaction between chlorine and lignin begins immediately in the mixer, and the reaction is completed in a chlorination tower designed to give the proper retention time. If chlorination is conducted at low temperatures (5 to 45°C) retention time may range between 15 and 60 minutes. Higher
temperatures reduce the time necessary to complete the chemical reaction. The main reaction by chlorine is an electrophilic substitution on aromatic rings, other reactions are cleavage of aryl-ether linkage i.e. demethoxylation and depolymerization (Kringstad, 1984). These reactions take place on any phenolic group. The reaction products are mainly polychlorinated aromatic rings (with chlorine). Chlorine also attacks cellulose, but this reaction occurs predominantly at pH 7, where unionized hypochlorous acid (HClO), which is the main chlorine species in solution (Ali and Sreekrishnan, 2001). To avoid excessive cellulose degradation, chlorination is carried out at pH <3.0. Under this condition chlorine selectively reacts with lignin and does little harm to cellulose fibres. Due to this the pH of the effluent is acidic in the range of 2.4 -3. The pollution load of this stream is not much higher because only acid soluble lignin is released. In the observation it was seen that the pollution load in the stream for various parameters was in the range of colour 400 - 800 PCU, COD 350 - 650 mg/l, BOD 150 - 225 mg/l, TS 1450 - 2000 mg/l, TDS 1360 - 1910 mg/l and TDS 60 - 125 mg/l.

Bleaching agents used to delignify chemical pulp, break lignin down into smaller, oxygen-containing molecules. These breakdown products are generally soluble in water, especially if the pH is greater than 7. These materials must be removed between bleaching stages to avoid excessive use of bleaching chemicals since many of these smaller molecules are still susceptible to oxidation. The purpose of extraction is to remove as much lignin from the pulp as possible to minimize the volume of more expensive bleaching chemicals (e.g., chlorine dioxide, hypochlorite, and hydrogen peroxide) needed in subsequent bleaching stages. Alkaline extraction removes the soluble coloured components and lignin released in the preceding delignification stage. Therefore the pH of the extraction unit was in between 8.5 - 10.5. After alkaline extraction, 80 to 90 percent of the lignin is removed due to which the parameter like colour, COD, BOD, TS, TDS and TSS were increased at alarming. It was observed that the colour was in the range of 2100 - 3000 PCU, COD was 1450 -1900 mg/l, BOD 280 - 400 mg/l, TS 1375 - 2360 mg/l, TDS 1130 - 2180 mg/l and TSS was about 220 - 330 mg/l.
In hypochlorite bleaching step, pulp is brightened as the chemical destroys and removes the residual lignin and lignin derivatives after chlorination and extraction. Hypochlorite is nonspecific, i.e., it attacks cellulose as well as lignin, therefore it requires careful control if a reduction in pulp strength is to be avoided. The hypochlorite treatment is carried out at pH in the range of 4-6. It was observed that the parameters like colour, COD, BOD, TS, TDS and TSS was in the range of 470 - 725 PCU, 490 - 900 mg/l, 240 - 420 mg/l, 1790 - 2550 mg/l, 1605 - 2360 mg/l, 185 - 260 mg/l respectively.

In combined bleach unit the effluent from chlorination, extraction and hypochlorite unit was collected. The characteristic of the effluent might vary because the flow from these units is not constant. Due to this, characteristics of the wastewater varies. Results showed that the pH varied from 5 - 7.5 i.e., acidic to neutral. The colour ranged from 1750 - 2550 PCU. Other parameters like COD, BOD, TS, TDS and TSS were varied from 1450 - 1950 mg/l, 350 - 620 mg/l, 2140 - 2540 mg/l, 1860 - 2290 mg/l and 190 - 280 mg/l respectively.

In the primary clarifier inlet, wastewater is collected from all the operations like pulping, bleaching and papermaking. The pollution load in this unit is comparatively less as compared to pulping and bleaching unit because the discharge gets diluted with the flow received from the paper making unit. The pH of the unit was in the range of 8.5 - 10. The pH of this unit is higher; this might be because the wastewater release from pulping and chemical recovery unit which contains high content of sodium hydroxide entered the PC inlet which increases the pH value of the total effluent in this unit. The other parameters i.e. colour increased because of the presence of lignin in the wastewater. The observed value for colour was in the range of 1350 - 2100 PCU. The COD of the primary clarifier inlet was in the range of 1050 -1500 mg/l. The organic load i.e., the BOD of the unit was in the range of 290 - 450 mg/l. The solids i.e., total solid, total dissolved solids and total suspended solids was in the range of 1750 - 2150 mg/l, 1360 - 1860 mg/l and 290 - 410 mg/l respectively.

Primary treatment is removal of suspended solids (85-95 %) from the effluent. This treatment is always accompanied by some reduction in BOD and COD. Usually two
principal methods are employed by the pulp and paper mill which are gravity sedimentation and dissolved-air flotation. Although flotation process is more efficient in removing solids but sedimentation is more commonly used by the pulp mills. Flotation process is expensive to operate whereas the sedimentation only requires little attention and maintenance (Smook, 1992). Alum dosage in the process of PC outlet, acts as a flocculating agent and simultaneously neutralizes the pH of the effluent. The observed value for pH was in the range of 6.5 -8 which is quite near to neutral. The range for colour was in between 680 -1130 PCU. The observed value for the COD was in the range of 580 - 970 mg/l. The value for BOD was in the range of 175- 250 mg/l. Total solids was observed and showed the value in the range of 1050 -1400 mg/l. The observed values for TDS and TSS was in the range of 930 - 1370 mg/l and 75 0 150 respectively.

After the wastewater has been through primary treatment process, it flows into the next stage of treatment called secondary. Secondary treatment is a purification process under contained and controlled conditions and in accelerated rates. The treatment is applying nature process by using the microorganisms (bacteria and fungi) under aerobic conditions. The microorganisms consume oxygen to convert organic waste into carbon dioxide and water (Smook, 1992; Lora and Escudero, 2000). Secondary treatment process can remove up to 90 percent of the organic matter in wastewater by using biological treatment processes. In the treatment process, the bacteria use oxygen from the air and consume most of the organic matter in the wastewater as food. As the wastewater passes down through the media, oxygen-demanding substances are consumed by the biomass and the water leaving the media is much cleaner. However, portions of the biomass also slough off the media and must settle out in a secondary treatment tank. The results showed that the observed pH value for the discharge from this unit varied from 6.8 - 8. The COD, BOD, TS, TDS and TSS value for the final discharge varied form 480 -700 PCU, 240 -350 mg/l, 15 - 28 mg/l 940 - 1280 mg/l, 910 - 1230 mg/l and 30 - 50 mg/l respectively. After observing the results, it was seen that the values of the effluent parameters were not within standard values proposed by the regulatory agencies (Table 3.10). The standard values provided by the regulatory
agencies showed that the pH should be in the range of 6.5-8.5. The value for COD is up to 250 mg/l. The standard decided for BOD is 30 mg/l. The colour value is not yet decided due to the unavailability of the efficient technology for the colour removal. The standard for the suspended solids and total dissolve solids is up to 50 mg/l and 2100 mg/l respectively.

**Table 3.10: Discharge standards for pulp and paper industry effluent**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Existing norms</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5-8.5 (LPM)</td>
</tr>
<tr>
<td>SS, mg/l</td>
<td>50 (LPM)</td>
</tr>
<tr>
<td>TDS, mg/l</td>
<td>2100</td>
</tr>
<tr>
<td>COD, mg/l</td>
<td>250 (LPM)</td>
</tr>
<tr>
<td>BOD, mg/l</td>
<td>30</td>
</tr>
<tr>
<td>Colour, PCU</td>
<td>Not defined</td>
</tr>
</tbody>
</table>

An efficient treatment technology is required to treat the effluent holistically. After observing the results from all the units, the final selected unit for the study was PC outlet because the pH of this unit was near to neutral therefore, further addition of chemical prior to treatment was not necessary. The temperature in PC unit was about 20 - 35°C which was favourable for the bacterial growth. While comparing the pollution load, this unit was lower as compared to other units. In other units, the wastewater was more concentrated and the temperature of the effluent stream was not suitable for the growth of the microorganisms. Therefore, treatment was difficult by using biological means. Another problem faced by these units was difficult to maintain the level of dissolve oxygen due to increased temperature. In PC outlet, the effluent was diluted by the effluent discharged from the paper manufacturing unit and the suspended solids were removed in the primary clarifier which resulted in decrease in the organic load. In view of above, the final unit selected was PC outlet for further experiments.
3.5. Conclusion

Effluent gee rated from seven units (chlorination, extraction, hypochlorite, combined effluent bleach plant, PC inlet, PC outlet and SC outlet) were analyzed and it was concluded that they have different loads depending upon the manufacturing processes. This pulp and paper mill has effluent treatment facility but improvements are still needed to increase their efficiencies for treatment of wastewater. This also indicated that there is a lot of scope in improvising the existing activated sludge system, which possibly could be done by utilizing the natural wealth of bacteria, specific for the particular pollution problem. On the basis of the results obtained, it was felt that the knowledge of the pollution index of each unit could form a base to devise appropriate strategies for mitigating potential environmental hazards arising due to these. It should also be borne in mind that each unit is complex with highly interactive operations and any perturbation in one unit may have a great impact on the ultimate discharge standards. Different units were analyzed for temperature, pH, lignin content, colour, COD, BOD, TS, TDS and TSS and it was concluded that the PC outlet was the best unit for treatment for further study.