CHAPTER - II

MATERIALS & METHODS

MATERIALS AND METHODS

1. STUDY AREA

In industrialized countries , the industrial wastes are mainly responsible for the pollution of rivers and nearest waterbodies, because the waste water effluents from industries are directly discharged into rivers without any treatment. The decomposition of these wastes by microorganisms results in the products which are unacceptable in taste and appearance as well as harmful to public health.

ICHALKARANJI is one of the industrialized city situated in Tahsil Hatkanangale in District Kolhapur. Due to widely spread textile industry , Ichalkaranji is known as " **Manchester of Maharashtra**". The manufacturing process of textile industry is mainly divided into two sectors. first is cloth manufacture which is dry process and second is chemical processing of cloth which is wet process. In Ichalkaranji, there are nearabout 40 to 50 textile chemical processing units. Out of these units, few are run on co-operative basis while others are private units. All these units require large volumes of water of high purity and generate equally large volumes of waste water as effluents which are highly variable with respect to quality and quantity. We have visited various private as well as co-operative processing units and selected the following processing unit for study. **The Yashwant Co-operative Processors Ltd. Industrial Estate, Ichalkaranji.** This process unit was established in 1963 to fulfill the needs of the local powerloom industry . It is registered under Maharashtra State Co-operative Societies Act., 1960 (Registration No. K.P.R. / P.R.G. (I) / 26 of 1963 dated 14.03.1963.

The co-operative society was formed by a group of people basically owners of powerlooms and a few members were from trading community. Late Mr. Dattajirao Kadam was the founder member of this processing unit. The society was formed to provide processing facilities to powerloom weavers to make the cloth marketable and superior for value addition. At present, the members of the society are 1293 which includes Co-operative societies, Individuals, Firms , Government of Maharashtra and all are mainly related with the business and activities of the textile industry.

The processing unit receives the grey woven cloth as a raw material produced on weaving machines i.e. handlooms, powerlooms & autolooms. This cloth is subjected to various treatments as various machines for increasing the market value of the fabric. This is called as wet processing or chemical processing of textile fabrics. This processing house is equipped with all types of machineries for processing cotton, synthetic and blended fabrics. This process house is confined mainly to Desizing , Bleaching, Mercerinzing, Dyeing, Printing and finishing processes. During last 38 years, process house had undertaken expansion schemes under which various machineries were added and rennovation of many machines was carried out.

With all these modifications, the present production capacity stands as under -

Sr. No.	Type of Processing	Monthly	Yearly
		Mtrs in lacs	
1	Bleaching	25.00	300.00
2	Calendering	12.50	150.00
3	Mercerizing	12.50	150.00
4	Dyeing	15.00	180.00
5	Printing	2.00	24.00
	Total Capacity	67.00	804.00

These processed fabrics are subjected to various finishing treatments.

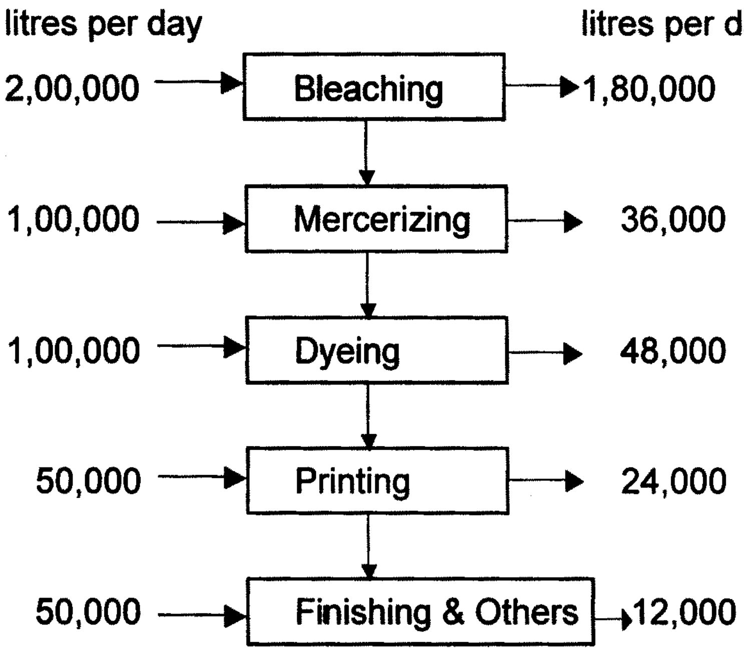
The working results of the last Six years are as under -

Sr. No	Details	1999 -00	2000 -01	2001 -02	2002 -03	2003 -04	2004 -05
1.	Cloth Processed (Mtrs in lacs)	224.58	179.50	180.42	192.00	202.00	210.00
2.	Processing Charges recieved (Rs. in lacs)	665.19	540.41	544.18	576.00	610.00	630.00
3.	Gross Profit (Rs. in lacs)	59.14	35.21	165.29	Under Assessment		
4.	Net Profit or Loss (Rs. in lacs)	-80.51	-118.65	+1.33	Under Assessment		
5.	Depreciation Provision	12.86	16.30	30.67	Under Assessment		

The various unit operations carried out in the selected processing unit are -

1. Bleaching
2. Mercerizing
3. Dyeing
4. Printing
5. Finishing.

Process flow Chart and effluent generations is as follows



Total Consumption of water 5,00,000

Total effluent 3,00,000

The quantity of cloth processed per day is 50,000 meters. The water requirement for all these operations is very large.

The details of various sections in this process house are as follows -

PLATE - I

FIG.1 Photograph of Bleaching section in the Processing unit.

FIG.2 Photograph of Mercerizing section in the Processing unit.

PLATE - 2

FIG.1 Photograph of Dyeing section in the Processing unit.

FIG.2 Photograph of Finishing section in the Processing unit.

PLATE - 3

FIG.1 Photograph of sample collection of Combined Effluent.

FIG.2 Photograph of Tank in which the Combined Effluent is discharged.

PLATE NO. 1

FIG.1

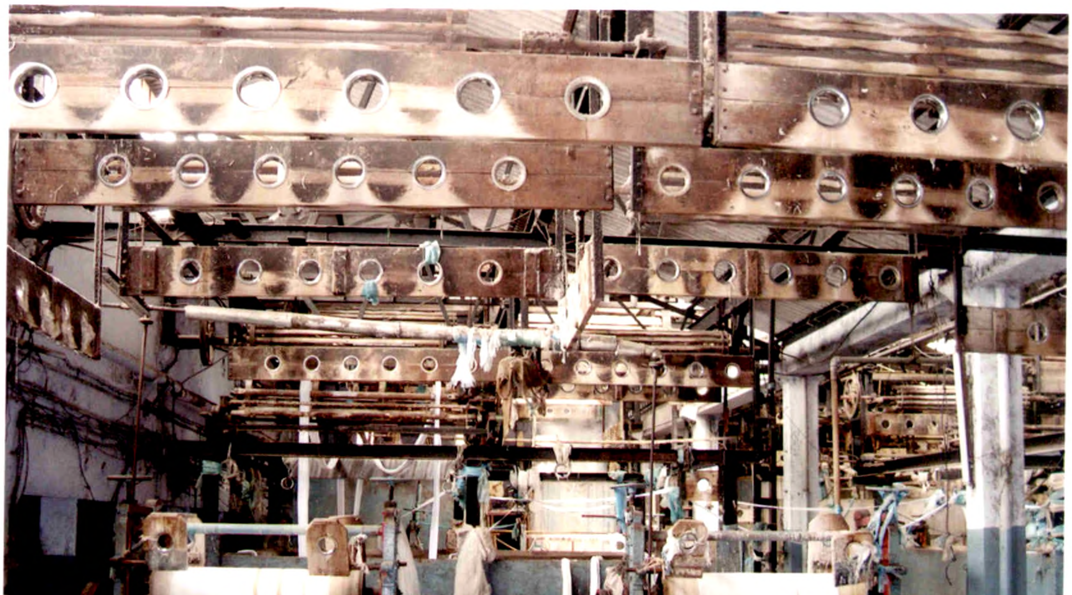


FIG.2

PLATE NO. 2

FIG.1

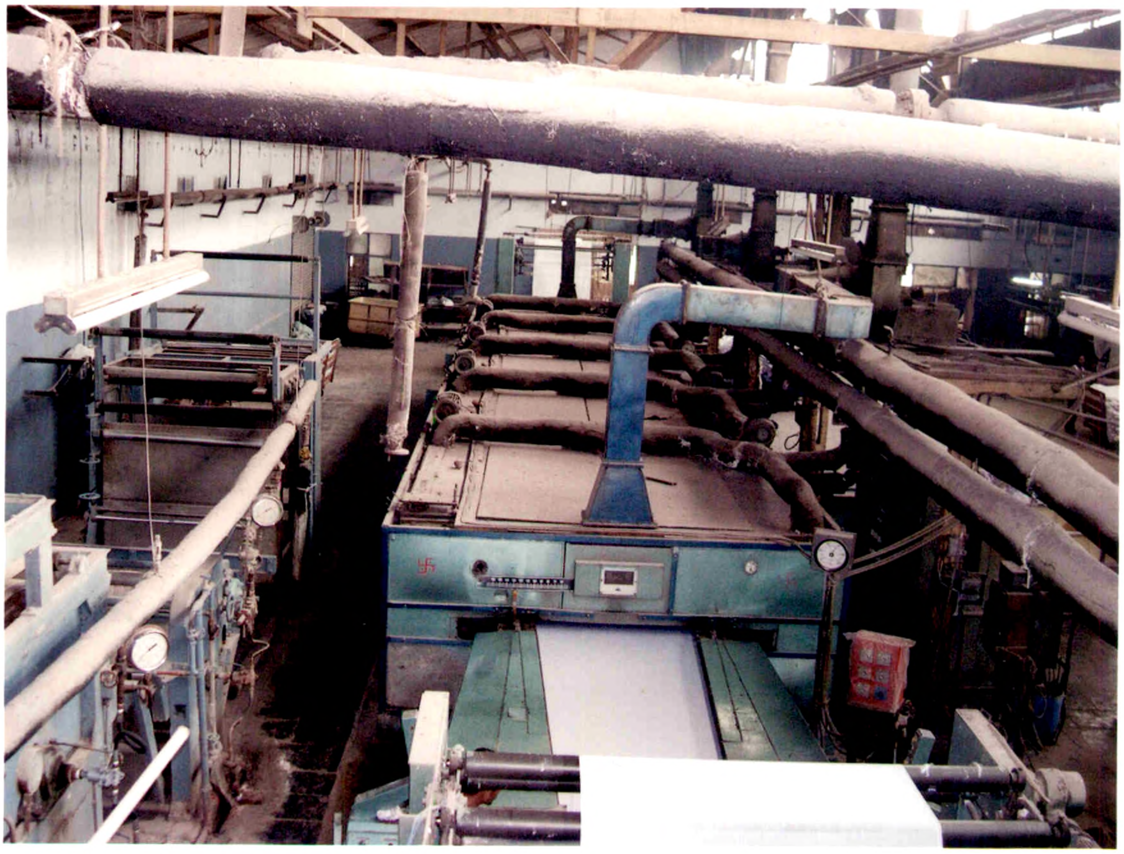


FIG.2

PLATE NO. 3

FIG.1

FIG.2

1. Desizing -

It is necessary to remove the sizing chemicals present in the grey cloth to make it suitable for further processing. Generally maize starch zymase is used as sizing agent. For removal of starch two methods are employed.

a} Acid treatment -

The gray cloth is treated with dilute sulfuric acid and washed well.

b} Enzyme treatment -

The cloth is steeped in bath and kept for 4 to 8 hours at 30°C to 40°C temperature. The enzymes hydrolyse starch and converts to readily soluble substances. Then cloth is subjected to mild acid treatment and rinsed with water.

2. Scouring -

Scouring is necessary to remove natural impurities and acquired impurities from the fabric. The method used for scouring is kier boiling. In a stainless steel vessels containing kiering liquor, fabric is heated under pressure at 90°C using steam. kiering liquor contains caustic soda (1 to 3 %) , Sodium silicate and sodium peroxide with small amount of detergents. The boiling is carried out for several hours (2 to 12 hours). Then fabric is rinsed well with water and it is continused until no brown colour remains in the rinse water.

3. Bleaching -

It is an essential finishing process used to remove natural colouring materials and to make the cloth white . For bleaching, alkaline hypochlorite or chlorine is used. Bleaching is usually followed by washing with fresh water and then treating wiht sodium bisulfite to remove traces of alkali and chlorine. Some finer fabrics are bleached by using sodium peroxide and hydrogen peroxide. Fabrics made from synthetic fibres are bleached using mild bleaching agents such as sodium hypochlorite. Optical brightners are also used to give fine lustre to the fabric.

4. Mercerizing -

Mercerization gives lustre, strength, dye affinity and abrasion resistance to fabric. The mercerized fabrics can easily be dyed. Rough varieties of fabric are directly sent for dyeing or printing after bleaching without mercerization.

In mercerization, fabric is treated with cold caustic solution for 1 to 3 minutes followed by thorough washing with water several times. The traces of alkali adhered to the fabric are removed by treating with dilute acid followed by rinsing with water.

5. Dyeing -

Dyeing is carried out by continuous process. In this method, the dye is transferred to the fabric by passing the fabric across rollers which are partially submerged in the dye solution. The moisture content of the fabric is reduced when the fabric passes through squeeze rollers in order to conserve the dyeing liquar and reduce the time required for drying. Various dyes are applied according to the requirement of the customer. The reactive dyes like coralene navy blue, coralene brown, coralene dark red, coralene scarlet, coralene yellow, coralene white , coralene orange, coralene violet, coralene green, coralene black, corazol yellow, corazol blue, corazol red, corazol violet, corazol black, HE brand reactive dyes are applied sometimes sulphur dyes, disperse dyes, vat dyes are also applied according to the colour and quality requirement of the customer. Acids and alkalies are added to increase the dye diffusion and to enhance reaction rate of the dye with the fibre in case of reactive dyes. When vat dyes and sulphur dyes are employed , sodium chloride and sodium sulphate is added to dye bath which acts as levelling agents to obtain more uniform dyeing. Urea is added with disperse dyes to increase the rate of dye diffusion. Organic solvents are sometimes used to increase the solubility of the dye and rate of dye penetration into the fibre.

6. Printing -

Printing is a process used to impart colour pattern to the cloth. Printing is carried out by usinf special type of screens or by passing the fabric through roller machines.

7. Finishing -

After dyeing or printing , fabric is passed for final finishing to impart smoothness and resistance to the cloth. For crease resistance and stabilizing finishing, urea and formaldehyde resins are used.

II) SELECTION OF SITE -

The important purpose of this study is to work out the water pollution caused by processing houses of textile industry in Ichalkaranji. These textile houses require large volumes of water for various unit operations and generate equal volumes of waste water as effluents. This waste water is disposed into the nearest water body and ultimately it is mixing with water of Panchaganga river. Hence it is the need of time to assess the water quality of industrial waste water effluents and try to search for the solution to this problem of water pollution.

III) PLAN OF PROPOSED WORK -

It was proposed to carry out Physico-chemical analysis of effluents from various sections of the processing unit. **The Yashwant Co-operative Processers Ltd., Ichalkaranji.**

Objectives of the study -

1. To find out and understand the facts about the causes of industrial pollution due to waste water effluents of textile processing unit.
2. To study and identify the reasons and problems for treatement of waste water effluents.
3. Physico-chemical analysis of waste water effluents from various sections of selected processing unit.
4. To compare the results of analysis with the standards available.

5. To interprete the results.
6. To suggest the preventive as well as remedial measures for the proper treatment of effluents.

IV) METHODOLOGY -

The analysis of the waste water effluents was carried out according to the standard methods of APHA (1992).

For preparation of all reagents AR grade chemicals were used.

1. Collection of Samples -

The waste water effluent samples were collected from the various sections of The Yashwant Co-operative Processers Ltd. , Ichalkaranji. The samples were collected from various sections like Bleaching, Mercerizing, Dyeing, Finishing as well as Combined effluents were also collected for analysis. For collection of samples, clean polythene containers of 5 litres capacity, polythene bottles of 1 litre capacity were used. Every time the containers were washed and rinsed with the waste water effluents samples and then samples were collected and carried to laboratory for analysis.

For Dissolved Oxygen and Biochemical Oxygen Demand, BOD bottles were used and samples were collected by siphoning to avoid aeration. Hot samples were cooled to atmospheric temperature after recording the temperature of effluent sample and then collected.

2. Parameters for analysis of Waste water effluents.

A. Physical Parameters -

1. colour.
2. Temperature.
3. Total Solids (TS).
    a. Total Suspended Solids (TSS).
    b. Total Dissolved Solids (TDS).

B. Chemical Parameters -

1. pH
2. Total Alkalinity (TA) Phenolphthalein alkalinity (PA).
3. Dissolved Oxygen (DO).
4. Chemical Oxygen Demand (COD).
5. Total Hardness (as $CaCo_3$).
6. Chlorides
7. Residual Chlorine.
8. Nitrates.
9. Nitrites.
10. Sulphates.
11. Oil and Grease.
12. Heavy Metals.

C. Biological Parameters -

1. Biochemical Oxygen Demand (BOD).

All the Experimental work was carried out at Deparment of Chemistry, Dattajirao Kadam Technical Institute of Engineering, Ichalkaranji, Dattajirao Kadam Arts, Science and Commerce

College, Ichalkarnaji and School of Environmental Sciences, Shivaji University, Kolhapur.

3. Analytical methods -

I. Physical Parameters -

1. Colour -

The colour of samples was observed visually and noted with reference to all samples collected from various sections of processing unit.

2. Temperature (°C) -

Temperature measurements were made at the time of sampling by using mercury filled thermometer. The reading was recorded by dipping the thermometer in effluent samples for sufficient time to record constant readings.

3. Solids (mg/L) -

a) Total solids (TS)

100 ml of unfiltered sample was evaporated in an initialy weighed evporating dish on hot plate at temperature below 100°C and then in oven for one hour at temperature 105°C and then weighed after cooling.

Formula

$$\text{Total Solids (TS)} = \frac{(A-B) \times 1000 \times 1000}{V}$$

A - Final Weight of the dish in g.

B - Initial weight of the dish in g.

V - Volume of sample taken in ml.

b) Total Dissoved Solids (TDS) -

TDS was determined by heating 100ml filtered sample in an initialy weighed evaporating dish on hot plate below 100°C and then in an oven at 105°C for one hour and then weighed after cooling -

Formula -

$$\text{Total Dissolved Solids (TDS)} = \frac{(A-B) \times 1000 \times 1000}{V}$$

A - Final Weight of the dish in g.

B - Initial weight of the dish in g.

V - Volume of sample taken in ml.

c) Total Suspended Solids (TSS) -

The Total Suspended Solids were determined by taking the difference between Total Solids and Total Dissolved Solids.

Formula -

$$TSS = TS - TDS$$

II. Chemical Parameters -

1. pH -

pH is a measure of hydrogen ion concentration which indicates the acidic or alkaline condition of waste water effluent. For pH measurements Digital pH meter was used with glass and calomel electrodes. Before measurement, pH meter was standardized by using standard buffer solution of pH = 4.0. Then pH of of effluent samples was recorded and the nature of the sample acidic or alkaline was decided.

2. Total alkalinity (TA) mg/L -

Total alkalinity was estimated by titrating the effluent sample wiht a strong acid 0.1 N HCl first to pH = 8.3 by using phenolphthalein and then further to pH between 4.2 to 5.4 with methyl orange as an indicator.

100ml sample was pipetted out in conical flask and 2 drops of phenolphthalein indicator were added. When the solution remained colourless then phenolphthalein alkalinity (PA) was recorded as zero and directly 2 drops of methyl orange were added to the same sample and then titrated with 0.1 N HCl until yellow colour changes to pink at the end point. This is the Total alkalinity (TA). When the colour of the sample was changed to pink after addition of phenolphthalein indicator, the solution was titrated with 0.1 N HCl until the colour disapears. This was recorded as Phenolphthalein alkalinity (PA). Then 2 drops of methyl orange were added and titration was continued until the yellow colour turned to pink at the end point. This reading was recorded as Total alkalinity (TA).

Formula -

$$\text{PA as CaCo}_3 = \frac{\text{A X Normality of HCl X 1000 X 50}}{\text{Volume of Sample in ml}}$$

$$\text{TA as CaCo}_3 = \frac{\text{B X Normality of HCl X 1000 X 50}}{\text{Volume of Sample in ml}}$$

A - Volume of HCl used with phenolphthalein in ml.

B - Volume of Total HCl used with phenolphthalein and methyl orange in ml.

3. Dissolved Oxygen (DO) mg/L -

Winkler's method was used for estimation of DO. For DO determination the effluent samples were filled in BOD bottles of 300 ml capacity immediately after collection of sample. Then 1 ml of each $MnSO_4$ and alkaline KI solution was added by dipping the pipette upto the bottom of the bottle for thorough mixing of reagent. A white coloured precipitate was formed due to manganous hydroxide which was oxidized to brown coloured compound. The BOD bottle was stoppered by using glass stopper carefully by avoiding any kind of bubbling and the contents were shaken well by inverting the bottle repeatedly. Then the bottle was kept for sometime to settle down the precipitate. At the time of titration, 1 to 2 ml of conc. H_2SO_4 was added. In strong acid medium manganic ions were reduced by iodide ions which get converted into iodine equivalent to the original concentration of oxygen in the sample.

50 ml of this solution was titrated with 0.025 N sodium thiosulphate solution by using starch indicator. At the end point initial dark blue colour turned colourless. Then the Do content was calculated by using formula -

$$\text{Dissolved Oxygen (DO)} = \frac{\text{(ml X N) of titrant X 8 X 1000}}{\left(V_2 \frac{(V1-V)}{V1}\right)}$$

V1 - Volume of sample bottle after placing the stopper in ml.

V2 - Volume of samle taken for titration in ml.

V - Volume of $MnSO_4$ and KI added.

4. Chemical Oxygen Demand (COD) mg/L -

Chemical Oxygen Demand is a measure of oxygen consumed during oxditaion of oxidizable organic matter by strong oxidizing agent.

20 ml sample was refluxed for two hours on hot plate carefully at 100°C temperature by adding 10 ml of 0.25 N potassium dichromate solution. A pinch of $HgSO_4$ to neutralize the effect of chlorides and Ag_2SO_4 as a catalyst. After reflux, the solution was cooled and then final volume was made upto 140ml by using distilled water. Then 2 to 3 drops of Ferroin indicator was added by thorough mixing and then solution was titrated with 0.1 N Ferrous ammonium sulphate. The same procedure was followed by using distilled water instead of waste water

effluent sample, simultaneously with same quantity of chemicals. The COD content was calcuated by using formula -

$$\text{COD} = \frac{(b-a) \times \text{N of Ferrous ammonium Sulphate} \times 1000 \times 8}{\text{Volume of Sample in ml}}$$

where a - volume of titrant with sample in ml.

b - volume of titrant with blank in ml.

5. Total Hardness mg/L -

Hardness is caused by the presence of calcium and magnesium ions in water, Therefore Hardness is measured as concentration of calcium and magnesium ions together. EDTA method was used to estimate to hardness of waste water effluent.

50 ml of effluent sample was titrated with 0.01 M EDTA solution by adding 100 mg Erichrome black-T indicator in presence of buffer solution. The end point was wine red to blue. The Total Hardness was calculated by using formula -

$$\text{Total Hardness as } CaCO_3 = \frac{\text{Volume of EDTA used in ml} \times 1000}{\text{Volume of Sample used in ml}}$$

6. Chlorides mg/L -

Silver nitrate reacts with chloride to form very slightly soluble white precipitate of silver chloride. At the end point free silver ions react with chromate to form silver chromate of reddish brown colour. 50 ml Sample was titrated with 0.02 N $AgNO_3$ by adding 5% Potassium chromate indicator until persistent red tinge appeared in the solution. The chloride content was calculated by using formula -

$$\text{Chlorides} = \frac{\text{Volume of titrant in ml X N of } AgNO_3 \text{ X 1000 X 35.5}}{\text{Volume of sample in ml}}$$

7. Residual chlorine mg/L -

Chlorine was added to the water for destroying the harmful microorganisms. The presence of excess chlorine intensities, gives the taste and odour to the waste water effluents. Chlorine is a strong oxidizing agent and liberates iodine from potassium iodide. This liberated iodine was equivalent to chlorine.

100 ml sample was titrated by adding 5 ml glacial acetic acid and 1 g of KI crystals with 0.025 N sodium thiosulphate solution using starch indicator. The end point was blue to colourless. The residual chlorine content was calculated by using formula -

$$\text{Residual Chlorine} = \frac{\text{Volume of titrant in ml X N titrant X 1000 X 35.5}}{\text{Volume of sample in ml}}$$

8. Nitrates mg/L -

For nitrate estimation, Brucine method was used. Nitrate and brucine react to produce a yellow colour.

In each 10 ml sample, 2 ml 30% NaCl solution, 10 ml conc. H_2SO_4 and 0.5 ml brucine reagent was added. Then this mixture was boiled for 20 minutes in hot water bath. Yellow colour was produced due to reaction of nitrate and brucine. The intensity of yellow colour was measured at 410 nm by using spectrophotometer.

A standard curve was prepared by using the dilutions of potassium nitrate as 0.1 to 1.0 mg/L at the intervals of 0.1 employing the same procedure used for effluent sample. By comparison method, the amount of nitrates was estimated.

9. Nitrites mg/L -

First of all, the colour of the sample was removed by using activated charcoal then after filtration 50 ml colourless effluent sample was used for estimation. In each sample, 1 ml of EDTA, Sulphanilic acid, alpha-naphthylamine hydrochloride and sodium acetate solution was added in sequence. A wine red colour was developed due to presence of nitrites. The intensity of colour was measured at 510 nm by using spectrophotometer.

A standard curve was prepared between 0.0 to 1.0 mg/L sodium nitrite at the interval of 0.1 employing the same procedure used for sample.

By comparison method, the amount of nitrite was estimated.

10. Sulphates mg/L -

For estimation of sulphates, Gravimetric analysis was carried out.

Sulphate was precipitated as barium sulphate in acidic medium by adding barium chloride solution.

In 100 ml of effluent sample, few drops of methyl red were added and the pH was adjusted to 4.5 to 5.0 by addition of HCl until the colour changes to orange. This solution was boiled. In this hot solution, $BaCl_2$ solution was added slowly for precipitating sulphates as barium sulphate. This precipitate was digested by heating at 80°C to 90°C for two hours. Then the precipitate was filtered through ashless whatman filter paper No. 42. The precipitate was washed with warm distilled water for removal of chlorides which was tested by $AgNO_3$ solution. Then the precipitate was dried in oven for one hour. Then ingnited in a previously weighed crucible. Then the crucible was cooled in dessicator and then weighed. This process of heating, cooling and weighing was repeated until the constant weight was recorded. From this weight of precipitate, the sulphate content was calculated by using formula -

$$SO_4 \text{ content} = \frac{\text{Weight of precipitate in mg X 411.5}}{\text{Volume of sample taken in ml}}$$

11. Oil and Grease mg/L -

For estimation of Oil and Grease, 200 ml sample was extracted with 25 ml petroleum ether by adding 10 ml sulphuric acid in a sepa rating funnel. The petroleum ether layer was evaporated in a previously weighed evaporating dish at temperature 40°C to 60°C on hot water bath. Then the final weight of the dish was recorded after cooling. By taking the difference between initial weight and final weight of the dish, the amount of Oil and Grease was calculated by using formula -

$$\text{Oil and Grease} = \frac{(A-B) \times 1000000}{V}$$

Where A - Final weight of the dish in g.

B - Initial weight of the dish in g.

V - volume of effluent sample taken in ml.

12. Heavy metals mg/L -

The quantitative and qualitative analysis for heavy metals was carried out by using Atomic Absorption Spetrophotometer.

III) BIOLOGICAL PARAMETERS -

1. Biochemical Oxygen Demand (BOD) mg/L -

BOD is a measure of degradable organic material present in water sample and it is defined as the amount of oxygen required by microorganisms in stabilizing the biologically degradable organic matter under aerobic condition.

First a dilution water was prepared by bubbing compressed air in distilled water for about 30 minutes by using aerator. 10 ml of effluent sample was diluted 1 litre by using this diluted water. In this solution 1 ml of each phosphate buffer, magnesium sulphate , calcium chloride and ferric chloride solution was added. This mixture was neutralized to pH = 7.0 by using 1 N NaOH or 1 N H_2SO_4. Then two sets of BOD bottles were filled with this mixture and bottles were stoppered carefully. One set of bottles was kept in incubator at 20°C for 5 days and another set was used to determine dissloved oxygen by winkler's method.

For blank, two BOD bottles were filled with dilution water and the procedure was followed only without effluent sample. One BOD bottle was kept for incubation simultaneously with the sample bottle and another was used to determine dissolved oxygen by the sample method employed for sample.

After 5 days incubation, both the bottles (sample and blank) were employed for estimation of Dissolved Oxygen.

The BOD content was calculated by using formula -

$$BOD = (D_0 - D_5) \times \text{dilution factor}$$

D_0 - Initial D0 in the sample.

D_5 - D0 after 5 days incubation.