CHAPTER 4

STUDIES ON
THE PHYSICOCHEMICAL
PROPERTIES
OF SUGAR FACTORY EFFLUENT

4.1 INTRODUCTION

India has been known as the original home of sugar and sugarcane. Indian mythology supports the above fact as it contains legends showing the origin of sugarcane. India is the second largest producer of sugarcane next to Brazil. Presently, about 4 million hectares of land is under sugarcane with an average yield of 70 tonnes per hectare. India is the largest single producer of sugar including traditional cane sugar sweeteners, khandsari and Gur equivalent to 26 million tonnes raw value followed by Brazil in the second place at 18.5 million tonnes. Even in respect of white crystal sugar, India has ranked No.1 position in 7 out of last 10 years. Sugar industry plays an important role in the economy of India by way of farming and creation of employment. The by-products of sugar mills are also used as raw materials in different industry. Some of the sugar factories in India are equipped with cogeneration of electricity and production of ethanol through its distillery unit. The general flow chart in a sugar factory manufacturing sugar, generating electricity and a distillery unit is given in figure 4.1.
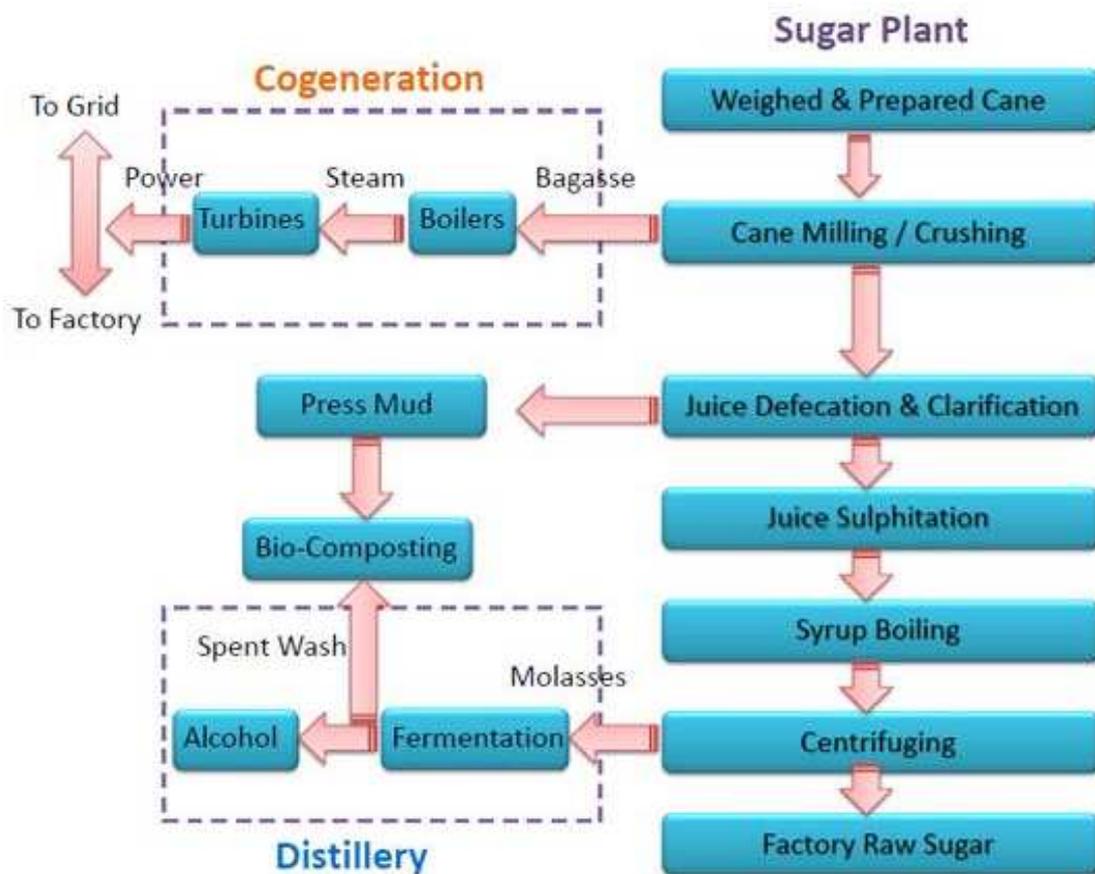

Figure 4.1 Sugar process flow chart

The main final products of sugar cane industry are crystalline sugar and bio-ethanol. The latter is obtained from the fermentation and distillation of sugar cane juice and molasses. Quantitatively, the most significant by-product is bagasse, the solid residue from sugar cane after juice extraction and stillage (also called vinnasse or dunder), the liquid waste effluent after the distillation process of sugar cane juice. Sugar mill with annexed alcohol distilleries generally release an average of 155 l of stillage and 250 Kg bagasse per 1,000 Kg of sugar cane to obtain 12 l of alcohol and 95 Kg of sugar. Bagasse can be used in boilers during combustion, while stillage is mainly disposed to field crops. The generation of waste water during the process is shown in the table 4.1. The waste water from mill house is usually contaminated with oil and grease. The spillage of oil and grease on floor of mill house is washed away during floor washing. The waste water generated from process and mill house is highly contaminated with process chemicals, which are being used at different processing stages.

Table 4.1: Waste water generation from each unit in a sugar industry.

Input	Unit House	Waste water generated
Sugar Cane	Mill housing	Waste water from bearing house of mills, contains suspended solids and oil contents, washing of floors.
Sugar Juice	Process house (Juice heaters/Evaporators/ Condensers/Crystallizers/ Rotary filters)	Washing of different components such as juice heaters /crystallizers, evaporators and water circulation through condenser.
Bagasse and Furnace oil	Boiler house (Final)	Waste water of wet scrubbers/blow down of boiler/flay ash particles.

Sugar industry is a larger water consuming industry. Water quantity required can vary due to the application of new technology and quality of raw material used. Sugar cane entering in the industry contains about 70-80 % moisture, as a result, excess water has to be disposed off, even with the water reuse (Sanjay, 2005). It has been observed that each ton of cane crushed should produce about 0.73 m3 of water if sugar and water are completely separated1. Mostly water is required in the sugar mills as mill floor washing, cooling water for barometric condensers, boiler fed water, lime preparation, for power pumps and evaporators.

According to Indian industry standards, water consumption varies from 1.3 to 4.36 m^3. The water generated is about 20% of the water requirement. The sugar industry with crushing capacity of 5000 Tons per day requires 10000 m3 /day of water. The mills generate the waste water in the ratio of 1:2 (Rao and Ranade, 1995).

The sugar industry waste water is characterized by its color, temperature of water, low pH, ash, and dissolved organic and inorganic matter of which 50% may present as reducing sugar (Khan et al, 2003). In addition to sugar mill waste water carry the constituents such as Biochemical Oxygen demand (BOD), Chemical Oxygen demand (COD), oil and grease and in the range which more than the CPCB standards in addition to considerable amount of chlorides, sulphates, nitrates, calcium, magnesium and various heavy metals (Saranraj and Stella, 2014). Hence sugar mills have a great environmental impact upon the surrounding environment. The change of water and soil chemistry is the main associated environmental impact of discharging sugar mill's effluent on an open water body. This can be understood as when we know the physical and chemical properties of the sugar mill effluent. Pertaining to available literature there is not a single article on assessment of sugar factory effluent from the study area. Hence, it was worth to make the efforts towards the analysis of sugar factory effluent that is released from Chopda Setkari Sahkari Sakhar Karkhana.

4.2 MATERIALS AND METHODS:

A) Survey of Study Area: Chopda Setkari Sahkari Sakhar Karkhana (Chopda Sugar Factory) is located in the vicinity of village Chahardi Tal: Chopda, District: Jalgaon Maharashtra state, located at the coordinates 21°12'41.51"N latitude and 75°15'08.47"E longitude and its MSL is 625 feet (Figure 4.1 and 4.2).

The site is surrounded by the sugar cane growing agricultural land in addition to cotton, banana, wheat and other grains. The available land is 132.85 acres (53.14 hectare) out of which 8.0 hectares for expansion including process, ETP and for other purposes like storage of Bagasse, Coal etc. and 11.7 hectares of land for development of Green Belt. This Land is flat whereby cutting-filling is being balanced.

Within 10 Km influence Zone, there are villages viz. Vele, Chahardi, Akulkheda, Akhatwade, Majrehol, Kajipura and Chopda city. Within this territory of sugar factory,

there is no Tropical Forest, Biosphere Reserve, National Park, Wild Life sanctuary and Coral Formation Reserve. Factory is also contributing in electricity generation.

Figure 4.2 Map of Maharashtra showing Chopda Sugar Factory

Figure 4.3 Satellite Image of Chopda Sugar Factory (Source: Google Earth)

B) Collection of sugar factory effluent:

The samples of sugar factory effluent were collected from mill house, process house and dumping site (final place) where spentwash is released at Chopda Setkari Sahkari Sakhar Karkhana (Chopda Sugar Factory) for consequently three years i.e. 2011-12, 2012-13, 2013-14 during operative phase of the sugar factory. Physical characterization of effluent was done on the spot while for physico-chemical analysis of effluent, soon after the collection samples were brought to laboratory under cold storage and kept in deep freezer at -20°C. These samples were assessed for their physico-chemical parameters as per the standard protocols described below in table 4.2.

Table 4.2. The analyzed parameters for the study of samples

Physical Parameters	Chemical Parameters	Physico-chemical Parameters
Color,	Chloride (Cl^-),	DO,
Odor,	Phosphate (PO_4^{3-}),	COD,
Temperature,	Sulphate (SO_4^{2-}),	BOD
pH,	Calcium and Magnesium	
EC,	Nitrate (NO_3),	
TDS,	Oil and Grease	

1) TEMPERATURE:

Impinging solar radiation and the atmospheric temperature bring about interesting spatial and temporal changes in natural waters, which manifest in setting up of convection currents and thermal stratification. Discharge of heated effluents also brings about thermal changes in natural waters. Temperature is basically an important factor for its effect on chemical and biological reactions in water. Rises in temperature of water accelerates chemical reactions, reduce solubility of gases, amplifies taste and odour, and elevates metabolic activity of organisms.

PROCEDURE:

Record the temperature of the water with the help of standard centigrade thermometer in ^{0}C. Effluent temperature was measured at sampling site by dipping thermometer for about one minute.

2) P^H (POTENTIO HYDROGEN):

P^H is the value expressed as the negative logarithm of the hydrogen ion concentration. The pH range is given between 0 to14; 7 being neutral, less than 7 being acidic and above 7 being basic or alkaline. Determination of pH is not very important since presence of neutral salts keeps it around 7.0. However, the pH of bicarbonates (HCO_3^-) waters is usually more than 7.5 and its determination may reflect the degree of sodicity in the sample.

PRINCIPLE:

pH is the negative logarithm of hydrogen ion concentration expressed as follows.

$$pH = -\log_{10} (H^+)$$

For pH below 7, the H^+ concentration exceeds OH^- and the range is acidic. When the OH^- concentration is more than $H^{+,}$ pH lies between 7 and 14 and the range is alkaline. The pH is a sort of voltage measurement and to cover the entire range $0 - 14$, a potential measurement in the range of $+420$ mv to -420 mv is needed since a potential difference of 59.1 mv is developed for a difference of one pH unit.

PROCEDURE:

The pH meter was adjusted to the known pH of buffer solution having pH 4 and 9.2. The pH was determined by taking about 100 ml of water in a 200 ml clean beaker and immersing the combined electrode of the pH meter in it. The pH was indicated on the dial.

3) ELECTRIC CONDUCTANCE (EC)

Electrical conductance is the ability of a substance to conduct the electric current. In water, it is the property caused by the presence of various ionic species like Ca^{+2}, Mg^{+2}, SO_4, Cl^- Its unit is Siemens per metre (Sm^{-1}) or dSm^{-1} (1000 µS/cm)

PROCEDURE

1.It was measured with the help of a conductivity meter. The instructions supplied by the manufacturer were followed.

2.Conductance depends on the area of the metallic electrodes and the distance between them. The factor used to convert the observed conductance into conductivity is called as the

\"cell constant.\" Cell constant of the 'conductance cell' is usually supplied by the manufacturer.

CALCULATION

Conductivity = observed condctunce x cell constant x temperature

4) ESTIMATION OF OXYGEN (Winkler's Iodometric Method)

Dissolved oxygen (DO) is one of the most important parameter of water quality directly affecting survival and distribution of flora and fauna in an ecosystem. The two main sources of DO are diffusion (from air) and photosynthesis, while major factors responsible for its depletion are biochemical oxidation and respiration by flora and fauna. Generally, in ecosystems free from pollution, high DO is found in euphotic zone, while its values are negligible in case of polluted water bodies due to presence of H_2S, NH_3, Nitrites, Ferrous ions etc. Thus, there is direct correlation between BOD and COD on one hand and DO on the other hand. Based on eutrophication status (organic enrichment level) the aquatic ecosystems are classified into Oligotrophic (nutrition poor) and eutrophic (nutritional enriched). In the case of oligotrophic water bodies DO have a narrow range as exhibited by orthograde oxygen curve (DO increase with depth), while in eutrophic systems clinograde oxygen curve (DO is more in surface and depletes sharply with the depth) is evident.

PRINCIPLE

The manganese sulphate reacts with the alkali KOH or NaOH to form a white precipitate of manganese hydroxide, which in the presence of oxygen oxidized to a brown colour compound. In the strong acid medium manganese, ions are reduced by iodide ions, which are converted into iodine equivalent to the original concentration of oxygen in the sample. The iodine can be titrated against thiosulphate using starch as an indicator.

REAGENTS

Sodium thiosulphate, 0.025N

28.42 gm of $Na_2S_2O_3$ $5H_2O$ were dissolved in boiled distilled water and made up the volume of 1 litre. 0.4 gm of borax or a pallet of NaOH was added as stabilizer. This was 0.1N stock solution. It was diluted to 4 times with boiled distilled water to prepar 0.025 N solution. It was kept in a brown glass stoppered bottle.

Alkaline potassium iodide solution

100gm of KOH and 50gm of KI were dissolved in 200 ml of distilled water.

Manganese sulphate solution

100 gm of $MnSO_4.4H2O$ was dissolved in 200 ml of boiled distilled water and the solution was then filtered.

Starch solution

g of starch was dissolved in 100ml of warm distilled water and a few drops of formaldehyde solution were added.

Sulphuric acid H_2SO_4, conc. (sp. gr.1.84)

PROCEDURE

1.A glass stoppered bottle (BOD Bottle) of known volume (100-300ml) was filled carefully with sample water at the collection sites on both rivers in morning once a week, avoiding any kind of air bubbling and trapping of the air bubble in the bottle after pacing the stopper.

2. 1ml of each MnSO4 and alkaline solutions (in case ,the volume of the sample is about 300 ml, instead of 1ml of reagents add 2ml solutions of each), were added to the sample water well below the surface from the walls. The reagents can also be poured at the bottom of the bottle with the help of special pipette syringes to ensure better mixing of the reagents with the sample. Separate pipettes were used for both reagents. A precipitate was appeared.

3. After placing the stopper and the contents were shaken well by inverting the bottle repeatedly. The bottles were kept for same time to settle down the precipitate. The bottles containing precipitate were brought to the laboratory for titrating the contents against Sodium thiosulphate

4. In the laboratory, 1-2 ml of conc H_2SO_4 was added in each bottle followed by vigorous shaking so as to dissolve the precipitate.

5. A part of the content (100 ml) was removed from the bottle and transferred to a conical flask for titration preventing any bubbling to avoid further mixing of oxygen.

6. The contents were titrated, within one hour of dissolution of the precipitate against sodium thiosulphate solution using starch as an indicator. At the end point, initial dark blue colour changes to colourless.

CALCUTATION

$$\text{Dissolved Oxygen, mg/ L} = \frac{(ml \times N) \text{ of titrant} \times 8 \times 1000}{V_1 - v}$$

When only a part of the contents has been titrated;

$$\text{Dissolved Oxygen, mg/L} = \frac{(ml \times N) \text{ of titrant} \times 8 \times 1000}{V_2 \ (V1 - v / V_1)}$$

Where, V_1 = volume of sample bottle after placing the stopper.

V_2 = volume of the part of the contents titrated.

v = volume of MnSO4 and KI added.

In oceanography, the unit ml/L is preferred over mg/L. It can be obtained by dividing the value in mg/L by 1.43.

5) BIOCHEMICAL OXYGEN DEMAND (BOD):

Biochemical oxygen demand is defined as the amount of oxygen required by microorganisms under test condition for complete oxidation of the organic matter in a water sample.

BOD is used as an index of organic pollution in water. More the oxidizable organic matter present in water, more the amount of oxygen required to degrade it biologically, hence more the BOD. The BOD test is widely used to determine 1) the degree of pollution in water, 2) the pollution load of wastewater and 3) efficiency of wastewater treatment plant.

PRINCIPLE:

To measure BOD, dissolved oxygen is supplied by diluting the sample with oxygen enriched distilled water and ideal conditions are created for aerobic bacteria by maintaining constant temperature (20^0C) and duration for bacterial action (5 days). Preliminary dilution and aeration of water sample usually necessary to ensure that not all the oxygen is consumed during incubation. Very high BOD values are recorded for polluted water and industrial waste.

MATERIALS : BOD incubator, BOD bottles, laboratory glassware and reagents.

1) All reagents used in determination of Dissolved oxygen i.e. Winkler's A: Manganese sulphate ($MnSO_4$), Winkler's B: Alkaline potassium iodide (KI), 0.025 N Sodium thiosulphate ($Na_2S_2O_3$), Starch indicator, and Concentrated Sulphuric acid (H_2SO_4)

2) BOD free water: Pass the deionised glass distilled water through a column of activated carbon and redistilled it.

3) Phosphate buffer: Dissolve 42.5 gm potassium dihydrogen phosphate (KH_2PO_4) in 700 ml water and add 8.8 gm sodium hydroxide. This should give a solution of pH 7.2, which should be checked. Add 2 gm ammonium sulphate and dilute to 1 liter.

4) Magnesium sulphate solution ($MgSO_4.7H_2O$): Dissolve 25 gm magnesium sulphate in 1 liter BOD free distilled water.

Table 4.3 Biological oxygen demand and the nature of water sample

No	Dilution factor	Sample	Dist. Water	BOD range	Nature of sample
1	1	1000	0	0 – 6	Unpolluted sample
2	2	500	500	4 – 12	--
3	5	200	800	10 – 30	Treated effluents
4	10	100	900	20 – 60	Treated effluents
5	20	50	950	40 – 120	--
6	50	20	980	100 – 300	Raw sewage
7	100	10	990	200 – 600	Raw sewage
8	200	5	995	400 – 1200	--
9	500	2	998	1000 – 3000	--
10	1000	1	999	2000 – 6000	Untreated
11	2000	0.5	999.5	> 6000	Industrial effluents

5) Calcium chloride solution ($CaCl_2$): Dissolve 27.5 gm anhydrous calcium chloride in 1 liter BOD free distilled water.

6) Ferric chloride solution ($FeCl_3.6H_2O$): Dissolve 0.125 gm ferric chloride in 1 liter BOD free distilled water.

7) Sulphuric acid (1N): Add 2.8 ml of concentrated sulphuric acid to 100 ml of BOD free distilled water.

8) Sodium hydroxide solution (1N): Add 4 gm of sodium hydroxide in distilled water and make the volume 100 ml.

9) Thiourea solution: Dissolve 500 mg of thiourea in distilled water and make the volume to 1 liter.

10) Preparation of dilution water: To prepare dilution water aerates the BOD free distilled water in a glass container for about half an hour. In one liter of this water, add 1 ml each of phosphate buffer solution (reagent C), magnesium sulphate solution (reagent D), calcium chloride solution (reagent E) and ferric chloride solution (reagent F).

PROCEDURE

1. The dilution water was prepared in a glass container by bubbling compressed air in distilled water for about 30 minutes.

2. One ml each of phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride solution were added for each litre of dilution water and mixed thoroughly.

3. The sample was neutralized to pH around 7.0 by using 1N NaOH or H_2SO_4.

4. Since the DO in the sample was likely to be exhausted; it is usually necessary to prepare a suitable dilution of the sample according to the expected BOD range.

5. Dilutions in a bucket or a large glass trough were prepared and mixed the contents thoroughly.

6. One set of the bottles in BOD was placed incubator at 25^0C for 5 days.

7. Immediately after the completion of 5 days of incubation, the DO in the sample bottles was determined.

8. Similarly for blank, two BOD bottles were taken for dilution water. In one, the DO content was determined and the other was incubated with the sample to determine DO after 5 days.

CALCULATION

$$BOD, mg/L = (D_0\text{-}D5) \text{ x dilution factor}$$

Where, D_0 =Initial Do in the sample

D_5 = DO after 5 days

6) CHEMICAL OXYGEN DEMAND (COD):

Chemically polluted water sample in which microbial oxidation is not possible due to the presence of toxicants/toxins, BOD can not be determined accurately. In such samples COD assesses the degree of organic pollution.

Chemical oxygen demand (COD) is the measure of oxygen required in oxidizing the organic compounds present in water means of chemical reactions involving oxidizing substances such as potassium dichromate and potassium permanganate.

PRINCIPLE:

Most of the organic matter is destroyed when boiled with a mixture of potassium dichromate and sulphuric acid producing carbon dioxide and water. A sample is refluxed with a known

amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate. The amount of dichromate consumed is proportional to the oxygen required to oxidize the oxidizable organic matter.

MATERIAL:

Reflux apparatus consisting of a flat bottom (250 – 500 ml), condenser (30 cm), heating mantle or hot plate and reagents:

A. Potassium dichromate ($K_2Cr_2O_7$; 0.25N): Dissolve 12.259 gm potassium dichromate previously dried at 103^0 for 24 hours in distilled water to prepare 1 liter of solution.

B. Silver sulphate ($AgSO_4$): Dry, powdered, AR.

C. Mercuric sulphate ($HgSO_4$): Dry, powdered, AR.

D. Sulphuric acid (H_2SO_4): Concentrated.

E. Ferroin indicator: Dissolve 1.485 gm of 1 – 10 phenonthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute to 100 ml. This indicator solution can be purchased already prepared.

F. Ferrous ammonium sulphate (Fe $(NH_4)_2(SO_4)_2.6H_2O$; 0.25N): Dissolve 98 gm of ferrous ammonium sulphate in distilled water, add 20 ml of sulphuric acid, cool and dilute to 1 liter. Standardize this solution daily against standard $K_2Cr_2O_7$ (reagent –A). To do this, dilute 10 ml standard $K_2Cr_2O_7$ (reagent –A) solution to about 100 ml with distilled water, add 20 ml concentrated H_2SO_4 and cool. Add 3 – 4 drops of ferroin indicator (reagent –E) and titrate with ferrous ammonium sulphate (reagent –F) until colour changes from blue green to a reddish blue (wine red) at end.

$$\text{Normality of reagent F} = \frac{VA \times 0.25}{VF}$$

Where, VA = Volume of reagent A (10 ml)

VF = Volume of reagent F used

PROCEDURE:

i. Take 20 ml of water sample in the flask of reflux unit.

ii. Add 10 ml of 0.25N potassium dichromate solution (reagent –A).

iii. Add a pinch of silver sulphate ($AgSO_4$) and mercury chloride ($HgCl_2$) or Mercury sulphate ($HgSO_4$) and 30 ml sulphuric acid.

iv. Attach condenser to the mouth of flask and heat the flask on a hot plate or heating mantle for at least 2 hours to reflux the contents.

v. Cool the flask, detach from unit and dilute its contents to about 150 ml by adding distilled water.

vi. Add 2 – 3 drops of ferroin indicator (reagent –E) and titrate against standard ferrous ammonium sulphate (reagent –F).

vii. End point – Blue green to reddish blue.

viii. Run simultaneously distilled water blank in similar manner.

CALCULATION:

$$\text{COD (mg/Liter)} = \frac{(B - A) \times N \times 1000 \times 8}{V}$$

Where, A = Titrant used against sample

B = Titrant used against blank

N = Normality of titrant (0.25)

V = Volume of the sample

7) TOTAL DISSOLVED SOLIDS (TDS)

Most of the salts and a variety of organic substances (except lipids) are soluble in water. Thus, a water sample, contains appreciable quantity of dissolved solids normally confer a degree of hardness to it. A large number of salts are found dissolved in natural waters. A high content of dissolved solids elevates the density of water and it influences osmoregulation of freshwater organisms, reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation, and industrial purposes.

PRINCIPLE

Total dissolved solids are determined as the residue left after evaporation of the filtered sample.

PROCEDURE

1. An evaporative dish was ignited at 550 +/- 50^0 C in a muffle furnace for about an hour, in a desiccator and its weight was noted.

2. The sample was filtered through glass fiber filter paper applying the suction.

3. 100 ml of this filtered sample was evaporated in preweighed evaporating dish on a water bath or a hot plate having temperature not more than 98^0C.

4. The residue was heated at 103- 105^0C in an oven for one hour and the final weight was taken after cooling in a desiccator.

CALCULATION

$$\text{TDS, mg/L} = \frac{A - B \times 1000 \times 1000}{V}$$

Where, A = Final weight of the dish in g,

B = Initial volume of the dish in g,

V = Volume of the sample taken in ml.

8) PHOSPHATES

Phosphorus occurs in natural waters and in wastewaters mainly as phosphates. Domestic and industrial effluents and agricultural runoff are major sources of phosphorus in water; hence its high concentration is indicative of pollution (Table 4.4). In water, phosphorus occurs both in inorganic and organic forms. Of the inorganic phosphorus, orthophosphate plays dynamic role by acting as the limiting nutrient. On precipitation orthophosphate gets trapped in the sediment, while under reducing conditions as obtained in most of the eutrophic ecosystems, some of the sedimentary phosphorus is recycled in soluble form. Though present in low concentration, phosphorus is one of the most important nutrients limiting growth of autotrophs and so biological productivity of the system. High phosphorus content causes algal growth, often as blooms, till nitrogen becomes limiting. Blue green algae, however, continue to grow as dominant algae because of their ability to utilize molecular nitrogen. Besides sedimentation, high uptake by phytoplankton is one of the reasons of fast depletion of phosphorus from water.

Table 4.4 Phosphate-phosphorus levels and effects

Total phosphate/ phosphorus	Effects
0.01-0.03 mg/L	Amount of phosphate-phosphorus in most uncontaminated lakes
0.025 mg/L	Accelerates the eutrophication process in lakes
0.1 mg/L	Recommended maximum for rivers and streams

PRINCIPLE

The phosphates in water react with ammonium molybdate and form complex heteropoly acid (molybdophosphoric acid), which gets reduced to a complex of colour in the presence of $SnCl_2$. The absorption of light by this blue colour can be measured at 690 nm to calculate the concentration of phosphates.

REAGENTS

A. Ammonium molybdate solution

1) 25.0 g of ammonium molybdate was dissolved in 175 ml of distilled water.
2) 280 ml of concentrated H_2SO_4 were added to 400 ml of distilled water and the cooled.
3) The two solutions (a) and (b) were mixed and diluted to 1 litre.

B. Stannous chloride solution

10 g of stannous chloride was dissolved in 100ml glycerol by heating on water bath for rapid dissolution.

C. Standard phosphate solution

4.388g of dried anhydrous potassium hydrogen phosphate K_2HPO_4 was dissolved in distilled water and made up the volume to 1 litre. This solution was diluted to 100 times (10-1000ml). This was standard phosphate solution containing 10mg P/L (1ml=0.01mgP).

PROCEDURE

1) 50 ml of filtered clear sample was taken in a clean conical flask. If the sample contained color and impurities, it was removed by adding a spoonful of activated charcoal and then filtered the sample.
2) 2 ml of ammonium molybdate was added and followed by 5 drops of $SnCl_2$ solution.
3) A blue colour was appeared. The reading was noted at 690 nm on a spectrophotometer using distilled water blank with the same amount of the chemicals. The reading after 5 minutes was noted but before 12 minutes of the addition of the last reagent.
4) The concentration of inorganic phosphorus was evaluated with the help of the standard curve.

9) SULPHATES

Sulphates are found in appreciable quantity in all natural waters, particularly high in arid and semiarid regions where natural waters in general have high salt content. Domestic sewage and industrial waste contribute sulphates to an aquatic ecosystem and hence high level of sulphate is an indication of pollution from organic matter. Biological oxidation of sulphur containing organic matter and precipitation in zones of high sulphur emission contribute sulphates to the water. Sulphates can be determined gravimetrically, colorimetrically, turbidimetrically or titrimetrically. Here, gravimetric method (Richards, 1954) is used.

PRINCIPLE OF GRAVIMETRIC METHOD

Sulphate is precipitated as barium sulphate in the hydrochloric acid medium by addition of barium chloride solution. The reaction is carried out near the boiling temperature. The precipitate is filtered, washed to remove the chlorides, dried pr ignited and weighed as $BaSO_4$.

Many substances interfere in performing this test. Suspended matter, silica, nitrate and sulphate lead to the positive errors where the results are on the higher side. Alkali metal sulphates cause the low results. Presence of other metals such as iron and chromium also yield low results due to the formation of metal sulphates.

REAGENTS

A. **Methyl red indicator**
B. 100 mg methyl red sodium salt was dissolved in distilled water to prepare 100 ml of solution.
C. **Hydrochloric acid** (1+1)
D. **Barium Chloride solution**

   100 g $BaCl_2.2H_2O$ was dissolved in distilled water to prepare 1 litre of solution. The solution was filtered through a filter paper before use.

E. **Silver nitrate – nitric acid reagent**

   20 g of $AgNO_3$ and 0.5 ml concentrated HNO_3 were dissolved in distilled water to prepare 500 ml reagent.

PROCEDURE

1. If the sample contained more than 25 mg/L of silica, it was removed prior to the analysis for sulphate.

2. For removal of silica, the suitable volume of sample was evaporated to dryness in platinum dish on a water bath. The residue in 1 ml of HCl (1+1) was dissolved by tilting and rotating the dish. Dry to contents again by evaporation and 2 ml of distilled water and 1 ml of HCl (1+1) were added and again evaporated to dryness on a water bath. 2 ml HCl was added and transferred it in hot water and filtered. The filter paper was washed having silica, several times with hot distilled water and the combined filtrate was collected.

3. The volume of the filtrate was adjusted so that 50 mg sulphate should be in 250 ml volume. If silica was present in less than 25 mg/L , there was no need of removal of it. And suitable volume of sample (100- 150ml) was directly taken for estimation of sulphate.

4. Few drops of methyl red were added to the sample and the pH was adjusted to 4.5 -5.0 by addition of HCl until the color changed to orange. Additional 1-2 ml of HCl was added.

5. The solution was boiled and warm $BaCl_2$ solution was added slowly in excess until the precipitation completes.

6. The precipitate was heated at 80-90^{0}C for at least 2 hours or more.

7. The precipitate was filtered through ashless filter paper (Whatman No.42) by adding some pulp of the same filter paper as aid for filtration.

8. The precipitate was washed repeatedly with warm distilled water until the filtrate was free from chloride which was tested by $AgNO_3$ solution. In the presence of chloride, $AgNO_3$ produced a white turbidity.

9. The filter paper containing precipitate was dried and ignited it in crucible at 800^{0}C for about 1 hour. It was cooled in desiccators and the precipitate of $BaSO_4$ was weighed.

CALCULATION

$$SO_4 \text{ mg/L} = \frac{\text{mg } BaSO_4 \text{ x } 411.5}{\text{ml of sample}}$$

10) CHLORIDE

Natural water bodies have a low chloride contents compared to bicarbonates and sulphates. High chlorides are found in inland saline lakes, estuaries and marine waters. In natural fresh waters high concentration of chlorides is considered to be an indicator of pollution due to domestic sewage and industrial effluents.

Chlorine is also used as a disinfectant in wastewater treatment plants and swimming pools. It is widely used as a bleaching agent in textile factories and paper mills, and it's an important ingredient in many laundry bleaches. Table 4.5 shows how chlorine affects fish and aquatic organisms. It is important to realize chlorine becomes more toxic as the pH level of the water drops. And it becomes even more toxic when it is combined with other toxic substances such as cyanides, phenols and ammonia.

Table 4.5 Effect of chlorine on fish and aquatic organisms

Total chlorine (gm/L)	Effect
0.006	Kills trout fry in two days.
0.01	Recommended maximum level for all fish and aquatic life.
0.01	Kills Chinook Salmon and Coho Salmon.
0.01-0.05	Oysters have difficulty pumping water through their bodies.
0.02	Maximum Brook and Brown Trout can withstand.
0.05	Maximum amount that can be tolerated by young Pacific Salmon in the ocean.
0.1	Kills most marine plankton.
0.25	Only the hardiest fish can survive.
0.37	Maximum fish can tolerate.
1.0	Kills oysters.

Free chlorine (chlorine gas dissolved in water) is toxic to fish and aquatic organisms, even in very small amounts. However, its dangers are relatively short-lived compared to the dangers of most other highly poisonous substances. That is because chlorine reacts quickly with other substances in water (and forms combined chlorine) or dissipates as a gas into the atmosphere. The free chlorine test measures only the amount of free or dissolved chlorine in water. The total chlorine test measures both free and combined forms of chlorine.

If water contains a lot of decaying materials, free chlorine can combine with them to form compounds called trihalomethanes or THMs. Some THMs in high concentrations are carcinogenic to people. Unlike free chlorine, THMs are persistent and can pose a health threat to living things for a long time.

PRINCIPLE

Silver nitrate reacts with chloride to form very slightly soluble white precipitate of AgCl. At the end point when all the chlorides get precipitated, free silver ions react with chromate to form silver chromate of reddish brown colour.

REAGENTS

A. **Silver nitrate**, 0.02N

   4 g of dried $AgNO_3$ (A.R) was dissolved in distilled water to make 1 litre of solution and kept in a dark bottle.

B. **Potassium chromate**, 5%

  5g of K_2CrO_4 was dissolved in 100ml of distilled water.

PROCEDURE

  a) 50 ml of sample was taken in a conical flask and 2 ml of K_2CrO_4 was added to the solution.

  b) The contents were titrated against 0.02 N $AgNO_3$ until a persistent red tinge appeared.

CALCULATION

$$\text{Chloride, mg /L} = \frac{(ml \times N) \text{ of } AgNO_3 \text{ x } 1000 \text{ x } 35.5}{ml \text{ of sample}}$$

11) CALCIUM AND MAGNESSIUM

Like calcium, magnesium is also found in all natural waters and its source too lies in rocks. It is generally in low concentration than calcium. Magnesium is a necessary constituent of chlorophyll without which no ecosystem could operate. Its high content reduces the utility of water for domestic use, while a concentration above 500 mg/L imparts water an unpleasant taste and renders it unfit for drinking purpose. High concentration of magnesium also proves to be diuretic and laxative.

PRINCIPLE

Calcium and magnesium form a complex of wine red colour with Erichrome Black T at pH 10.0. The EDTA has got a stronger affinity for Ca^{++} and Mg^{++}; the former complex is broken down and a new complex of blue colour is formed. The value of Mg^{++} can be obtained by subtracting the value of calcium from the total of $Ca^{++} + Mg^{++}$.

REAGENTS

A. **EDTA solution**, 0.01 M

   3.723g of disodium salt of EDTA was dissolved in distilled water to prepare 1 litre of solution. The solution stored in polythene or Pyrex bottle.

B. Buffer solution

 i) 16.9 g ammonium chloride (NH_4Cl) was dissolved in 143 ml of concentrated ammonium hydroxide (NH_4OH).

 ii) 1.179 g of disodium EDTA and $0.780.7H_2O$ were dissolved in 50 ml distilled water. Both (a) and (b) solutions were mixed and diluted to 250 ml with disttiled water.

C. **Erichrome Black T** (Solochrome Black T) indicator

  0.40 g of Erichrome Black T was mixed with 100g NaCl (A.R.) and grounded.

PROCEDURE

1.Find out the volume of EDTA used in calcium determination.

2.Also find out the volume of EDTA used in hardness (Ca^{++} +Mg^{++}) determination with same, volume of the sample as taken in the calcium determination.

CALCULATION

   a) Mg^{++}, mg/L = $\dfrac{Y–X \times 400.8}{\text{Volume of sample} \times 1.645}$

        Where, Y = EDTA used in hardness determination

                X = EDTA used in calcium determination for the same

                 volume of the sample.

   b) Mg^{++} ,mg/L = total hardness(as mg/L $CaCO_3$) –
                Calcium hardness (as mg/L CaCO3) x 0.244

       Where, Calcium hardness (as mg/L $CaCO_3$) = Ca, mg/L x 2.497

12) NITRATE (NO_3):

Nitrate is the highest oxidized form of nitrogen and in water its most important source is biological oxidation of nitrogenous organic matter like domestic sewage, agricultural runoff, metabolic waste of aquatic community and dead organic matter. Nitrifying bacteria, *Nitrosomonas* and *Nitrobacter* play significant role in oxidation of such organic matter.

Certain nitrogen fixing bacteria, *Azobactor* and algae, *Anabaena* and *Nostoc* have capacity to fix molecular nitrogen in nitrates. In ground water nitrates may find way through leaching from soil and at times by contamination. The high concentration of nitrate in water is indicative of pollution. This is important plant nutrient, when present in excess it causes ubiquitous growth of algae, often present in blooms. High nitrate content may cause blue-baby disease.

PRINCIPLE

Nitrates (NO_3) react with phenol disulphonic acid producing nitro derivatives, which in alkaline solution develop yellow colour. The OD of sample is directly proportional to concentration of nitrate.

MATERIAL

A. Phenol disulphonic acid: Dissolve 25 gm of white phenol in 150 ml of concentrated sulphuric acid and further add 85 ml of concentrated sulphuric acid. Heat for about 2 hours on a water bath, cool and keep the solution in a dark bottle.

B. Potassium hydroxide solution (KOH; 12N): Dissolve 336.5 gm of potassium hydroxide in distilled water to make the volume 500 ml.

C. Standard nitrate solutions: Dissolve 0.722 gm of anhydrous potassium nitrate in distilled.water to prepare 1 liter of stock solution. This stock solution contains 100 mg nitrate per liter.

Prepare standard nitrate solutions of various concentrations preferably in the range from 0.0 to 1.0 mg/Liter by diluting stock solution with distilled water.

PROCEDURE

i. Evaporate 25 ml water sample preferably overnight in a hot air oven (or hot water bath) adjusted at 50^0C.

ii. Add 0.5 ml of phenol disulphonic acid (reagent A) to the residue and dissolve the latter with the help of a glass spatula.

iii. Add 5 ml of distilled water and 1.5 ml of potassium hydroxide solution (reagent B). Stir for mixing.

iv. Take the supernatant of yellow colour and read its absorbance on spectrophotometer at 410 nm. Use distilled water as blank.

v. Process the standard nitrate solutions (reagent C) in similar manner and note the absorbance for each.

vi. Plot a standard curve between absorbance and concentration of various standard solutions. Deduce the value of nitrate in the water sample by comparing the absorbance of sample with the standard curve and express the result in mg/L.

13) OIL AND GREASE:

The method applied for quantitative determination of Oil and Grease (hexane extractable material, HEM) in the sugar factory effluent. Oil and Grease provides a measure of hexane extractable non-volatile oils and greases which may be of either petrogenic or natural origin.

Procedure:

Sugar factory effluent was acidified to pH < 2 using HCL or H_2SO_4 and extracted three times with hexane (or "hexanes") in a separatory funnel. The extract was dried with sodium sulfate, the solvent and any volatile components were evaporated, and the residue was weighed.

Samples were sequentially extracted with three aliquots of hexane in a separatory funnel. Samples were shaken vigorously for 2 minutes per extraction. The first aliquot of hexane was used to rinse the sample container so that its entire contents were transferred to the extraction vessel. The ratio of solvent to sample should be no less than 1:20, i.e. 50mL of hexane (per extraction) per 1L of sample. The solvent extracts were passed through a drying funnel containing anhydrous sodium sulfate and combined together. The extract was evaporated to dryness at ambient temperature (~20-25ºC). Following evaporation, residual water, solvent, and other volatiles were removed by heating in an oven at 50-60ºC for 30-60 minutes or by continued evaporation at ambient temperature, prior to gravimetric determination of the residue using a balance.

4.3 RESULT AND DISCUSSION:

Among the various industries, sugar mill is one of the most important agro based industries in India. It plays a major role in creating rural economy of the country as a whole. The sugar mill operates for 4 to 6 months per year as per the production and availability of sugar cane. A considerable amount of waste water is released during crushing of sugar cane. These waste waters are disposed into nearby water bodies and they are being used for irrigation. The discharge of effluent directly or indirectly into water bodies or on soil is causing a serious problem of water pollution resulting in severe damage to the flora and fauna and

environmental degradation (Pande, 2005). A significant large amount of waste is generated during the manufacture of sugar and contains a high amount of production load particularly in items of suspended solids, organic matters, effluent, sludge, pressmud and bagasse (Solomon, 2008).

Sugar factory effluent produces obnoxious odour and unpleasant color when released into the environment without proper treatment. Farmers have been using these without proper treatment and found that soil health were reduced (Kisku et al, 2000).

Generally, the effluent is generated from mill house, waste water from boiling house, waste water from boiler blow- down, condenser cooling water and soda and acid wastes (Kolhe et al, 2000). Indian sugar mills generate 0.16-0.76m^3 of waste water for every tonnes of cane crushed by them. The pollution standards stipulate that BOD of waste water should be less than 30 mg/L for disposal into inland surface waters and less than 100 mg/L for disposal on land. Whereas, the combined sugar mill waste water had a BOD of 1,000 to 1,500 mg/L (Adnan et al, 2010). Nath and Sharma (2004) reported that the untreated sugar mill effluent is toxic to plants when used for irrigation.

In the Chopda sugar factory, every year about 2 lac tones of sugar cane has been crushed that produced about 250 tones sugar during one operative phase. Every day about 1200 to 1500 Metric ton cane sugar is crushed. Regarding water consumption and effluent generation in Chopda sugar factory, about 1,000 liters of water consumed for a tonne of sugar cane crushed, which generated about 500-650 liters of waste water during one crushing season. Finally the effluent of Chopda sugar factory was released in big sized digs/pits made in the adjoining soil in the vicinity of sugar factory.

For physical and chemical analysis of samples collected from Chopda sugar factory, a number of sophisticated instruments were used and standards methods were followed. To measure the effluent quality of the collected samples the following analysis were performed in the PG Research laboratory of Dept of Zoology, ASC College, Chopda. The results of analyzed parameters are given in the Table 4.6 and its statistical significance evaluated by GraphPad Prism with one way ANOVA is mentioned in Table 4.7. The F-test is used for comparisons of the components (physic-chemicalparameters) between rows and columns.

Physico-chemical analysis of Chopda Sugar Factory Effluent:

Colour: According to the present study, the colour of the Chopda sugar factory effluent was dark brownish. Colour is very important factor for aquatic life for making food from sun rays. There is reduction in the photosynthesis activity of organisms due to dark coloration and it also affects other parameters like temperature DO and BOD etc. The dark brownish color of spentwash inhibits the growth of photosynthetic organisms (Anil Kumar et al, 2003).

Odour: During the course of study, the effluent released from Chopda sugar factory had a sugar cane juice like smell that indicated the presence of sugar residues in the waste water. In addition, an unpleasant and decaying smell dominated at digs containing spentwash (Doke et al, 2011).

Temperature:

The effluent temperature plays an important role in making an effect on certain chemical and biological reactions taking place in water which affects organism and inhabitation of aquatic media. It depends upon season, time of sampling etc. The water discharged from the industry which has generally high temperature, affects the land adversely. The temperatures of Chopda sugar factory effluent samples ranged between 42.1°C to 45.4°C which were remained higher than the BIS values of effluent's temperature (40°C). There was decreasing trend in the temperature of effluent from mill house followed by the process house and comparatively lower temperature was recorded in effluent at dump site which might be due to progressive increase in the volume of the effluent as one move from mill house to spentwash storage digs. The solubility of oxygen decreases as the temperature and pressure increases, warm waste water tends to lower the value of the dissolved oxygen, which further aggravates environmental problems (Ayyasamy et al, 2008)..

pH

In the present investigation the lower and higher pH values of effluent were recorded as 4.43 and 6.85 respectively. The pH of effluent showed progressive increase from mill house to process house and finally to spentwash but it never crossed the pH 7. Relatively low pH values of effluent samples were due to use of phosphoric acid and Sulfur dioxide added during cleaning of sugar cane juice. pH is one of the important biotic factor that serves as index for pollution. If such spentwash is used for irrigation for a longer period the soil becomes acidic resulting in poor crops growth and yield (Nath and Sharma, 2002). The

values of pH are due to the change in the manufacturing process of each industry with remelt sulphitation process in which acidic compounds of sulphur are formed, whereas there is also use remelt carbonation. Several chemicals are used for coagulation of impurities. Calcium hydroxide is used to clarify and increase in pH of juices.

Electric Conductance (EC)

The conductivity of a solution of water is highly dependent on its concentration of dissolved salts and sometimes other chemical species which tend to ionize in the solution. Electrical conductivity of water samples is used as an indicator of how salt-free or impurity-free the sample is; the purer the water, the lower the conductivity (Pande, 2005). EC values in samples of effluent of Chopda sugar factory fluctuated between 2.02 to 4.78 dSm^{-1}during three years of study. All the time EC values remained greater than the standard value described by BIS (clean water may have EC values 0.005 to 0.5 dS/m).

Dissolved Oxygen (DO)

The analysis of DO is very important in water pollution control as well as waste water control. Aquatic ecosystem totally depends on DO, various biochemical changes and its effects on metabolic activities of microorganism were very well documented. Its presence was essential to maintain variety of forming of biological life in water and effect of water discharge in water body are largely determined by oxygen balance of the system (Deshmukh, 2001). According to the BIS standard, the DO of the effluent should be within the range 4 to 6 mg/L. In the present investigation, the DO of Chopda sugar factory effluent samples were fluctuated between lower 1.22 to maximum 2.59 mg/L these values were sufficiently lower than the values described by Bureau of Indian standard. Comparatively lower DO values were recorded in mill house and process house effluent while higher DO was found in spentwash samples, which might be due to rainfall that lowered the temperature of the effluent and favored the amount of oxygen to be dissolved in the effluent. In three years of the study, the DO values were higher during 2013-14 than that of previous two years because more and continuous rainfall that reduces the temperature of the spentwash that improved the conditions for more DO.

Biochemical Oxygen Demand (BOD)

BOD is defined as amount of oxygen required by microorganism while stabilizing biological decomposable organic matter in water under aerobic conditions. The biological oxidation is

very slow process, during oxidation organic pollutants are oxidized by certain microorganism into carbon dioxide and water using dissolved Oxygen. Hence lowering in dissolved oxygen value is the measure of BOD relation (Jadhav et al 2013). In the present investigation, the BOD values of the Chopda sugar factory effluent were fluctuated from lower 365 to maximum 560 mg/L. BOD values found were lower during the year 2013-14 in samples of spentwash as compared to that of previous two years. According to BIS, the BOD should not exceed the 50 mg/L.

Table 4.6 Physico-chemical properties of Chopda sugar factory effluent during three years of operational period.

Parameter	Operative period during 2011-12			Operative period during 2012-13			Operative period during 2013-14		
	Mill	Process	Final	Mill	Process	Final	Mill	Process	Final
Temp (^{o}C)	45.4 ± 0.6	43.7 ± 0.3	42.3 ± 0.4	44.9 ± 0.3	44.2 ± 0.2	42.6 ± 0.4	44.7 ± 0.2	43.7 ± 0.4	42.1 ± 0.5
pH	4.54 ± 0.03	5.25 ± 0.04	6.28 ± 0.03	4.43 ± 0.02	5.46 ± 0.05	6.45 ± 0.02	4.35 ± 0.03	5.42 ± 0.05	6.85 ± 0.07
EC (dS·m^{-1})	2.23 ± 0.02	3.29 ± 0.04	4.21 ± 0.06	2.02 ± 0.02	3.37 ± 0.03	4.45 ± 0.05	2.20 ± 0.06	3.36 ± 0.05	4.78 ± 0.08
DO (mg/L)	1.24 ± 0.03	1.58 ± 0.04	2.41 ± 0.02	1.22 ± 0.04	1.34 ± 0.05	2.28 ± 0.02	1.32 ± 0.05	1.67 ± 0.05	2.59 ± 0.03
BOD (mg/L)	365 ±21.3	410 ±35.5	560 ±15.9	358 ±14.7	405 ±22.5	496 ±18.4	386 ±22.7	417 ±14.6	488 ±12.5
COD (mg/L)	742 ±15.4	870 ±25.6	1034 ±33.7	649 ±18.8	790 ±31.7	1155 ±44.5	695 ±15.4	952 ±25.6	1245 ±22.5
TDS (mg/L)	425 ±9.5	634 ±14.7	710 ±18.3	345 ±8.6	569 ±12.4	790 ±14.5	455 ±4.8	635 ±19.2	540 ±12.6
Phosphates (mg/L)	4.32 ±0.5	5.24 ±0.2	6.17 ±0.6	3.98 ±0.2	5.45 ±0.4	6.54 ±0.7	4.21 ±0.5	5.65 ±0.4	5.23 ±0.3
Sulphates (mg/L)	256 ±5.8	310 ±12.9	468 ±14.8	290 ±7.2	315 ±19.3	490 ±16.4	242 ±6.4	348 ±17.3	415 ±18.5
Chlorides (mg/L)	174 ±2.7	210 ±3.5	265 ±4.3	158 ±2.7	242 ±4.8	276 ±8.5	160 ±5.6	200 ±5.7	249 ±4.3
Calcium (mg/L)	34 ±6.3	47 ±4.6	69 ± 8.8	29 ±7.9	53 ±8.7	79 ± 5.5	31 ±6.3	56 ±4.6	52 ± 8.8
Magnesium (mg/L)	18 ±3.4	21 ±3.7	29 ±5.8	12 ±2.5	24 ±2.3	31 ±4.3	15 ±1.3	22 ±1.8	17 ±2.6
Nitrates (mg/L)	4.6 ±0.2	5.3 ±0.6	9.7 ±0.4	3.8 ±0.3	6.5 ±0.8	10.7 ±0.5	4.4 ±0.5	5.3 ±0.5	7.1 ±0.4
Oil/Grease (mg/L)	21 ±1.8	58 ±4.2	123 ±9.6	18 ±1.8	66 ±4.3	142 ±9.6	37 ±2.5	63 ±5.9	158 ±11.5

Figures are Mean ± SD of six observations.

Table 4.7 Stastical analysis of physico-chemical parameters of Chopda sugar factory effluent

One-way ANOVA					
Source of Variation	% of total variation	P value	P value summary	Significant?	
Row Factor	93.18	< 0.0001	****	Yes	
Column Factor	2.061	< 0.0001	****	Yes	
ANOVA table	**SS**	**DF**	**MS**	**F (DFn, DFd)**	**P value**
Row Factor	8.910e+006	13	685414	F (13, 104) = 156.6	P < 0.0001
Column Factor	197122	8	24640	F (8, 104) = 5.631	P < 0.0001
Residual	455081	104	4376		

COD

The chemical Oxygen demand test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test which is used to measure pollution of domestic and industrial waste. The quality of effluent is measured in term of quality of oxygen required for oxidation of organic matter to produce carbon dioxide and water (Baruah et al, 1993). It is a fact of all organic compounds with few exceptions that they can be oxidized by the action of strong oxidizing agents under acidic conditions. COD is useful in pinpointing toxic condition and presence of biological matters. In the present investigation the COD values of the Chopda sugar factory effluents were within minimum of 649 to maximum of 1245 mg/L. The COD values remained appreciably higher as compared to BIS standard (250 mg/L). This indicated the presence of high organic pollutants in the sample.

Total Dissolved Solids (TDS)

The estimated values of TDS in the effluent represent the colloidal form and dissolved specters. The probable reason for the fluctuation of value of total solids and subsequent the value of dissolved solid is due to convent collision of the colliding particles. The rate of collision aggregated process is also influenced by pH of this effluent. In the rainy season less concentration of total dissolved solids are obtain due to dilution of waste effluent with rain water (Hunachew and Banerjee, 2011). This resembles the finding in the present investigation that TDS value in spentwash of Chopda sugar factory was higher (790 mg/L) during sampling year 2012-13 due to drought like condition and lower TDS values (540 mg/L) in spentwash during year 2013-14 due to more and consistency in the rain. Overall in three year of study the TDS values of spentwash samples were much higher compared to BIS (500 mg/L).

Phosphates

The phosphate content in the spentwash of Chopda sugar factory remained higher as compared to mill and process house effluent. The values of phosphates were fluctuated within the range of 4.21 to 6.54 mg/L and the phosphate value was less in year 2013-14 as compared to previous two years of sampling which was due to dilution of spentwash due to more rainfall. Overall, the phosphate values remained higher as compared to values mentioned by BIS.

Sulphate

Sulphate can also be produced by factorial or an oxidizing action as in the oxidation action or in the oxidation of sulphur compounds. Sulphur itself has never been limiting factor in aquatic system, the normal levels of sulphate are more than adequate to meet plants needs. Odors conditions are easily greater when water is over loaded with organic wastes which reduce the oxygen, SO_4 an electron acceptor is often used for the breakdown of organic matters and produces H_2S causing bad smell of rotten egg (Adnan et al, 2010). In the present investigation sulphate content in spentwash samples of Chopda sugar factory was varied in the range of 242 to 490 mg/L during three years of study. According to BIS, the sulphate should not exceed the 100 mg/L. High SO_4 amount in both the effluents is attributed to the use of sulphur during crystallization

Chlorides

The presence of chloride in natural water is attributed to dissolution of salt deposit, discharge of effluents from chemical industries and oil well operations (Sanjay K, 2005). In the present study chlorides content in effluent samples of Chopda sugar factory fluctuated within lower 158 mg/L to maximum 276 mg/L. These values were well within the limits of values described by BIS.

Calcium and Magnesium

In the present investigation, the maximum concentration of Calcium and Magnesium in Chopda sugar factory effluent was 79 mg/L and 31 mg/L respectively while lower values of the same were 29mg/L and 12 mg/L respectively. The concentration of Calcium and Magnesium shown increasing trend in the samples from mill house to digs containing spentwash during 2011-12 and 2012-13 but in year 2013-14, the spentwash was diluted due to more rainfall and hence the values for Calcium and Magnesium were decreased. In both

the cases, the estimated values in all type of samples collected from Chopda sugar factory were remained higher as compared to that are ascertain by BIS.

Nitrates

The samples of waste water collected from Chopda sugar factory during three years of study shown increasing trend from mill house, followed by process house and finally in spentwash digs so far its nitrate content was concerned. The maximum value of nitrate was 10.7 mg/L and the lower value was 4.4 mg/L in the effluent sample. On comparing the percent change in the nitrate content from mill house to spentwash samples, it was found that this change was more during year 2011-12 (2.1%) and 2012-13 (2.8%) but in year 2013-14 due to dilution effect of rain water, the percent change (1.6%) was reduced. Nevertheless, the nitrate content in all the samples was lower in accordance to BIS.

Oil and Grease (O & G)

On analyzing the wastewater samples collected from Chopda sugar factory for its oil and grease content, it was noted that oil and grease content fluctuated within lower 18 mg/L and higher 158 mg/L during three years of study period. These figures were always high in accordance with the BIS (10mg/L). The final effluent had higher values of O&G in all samples which indicated the improper maintenance of equipments and leakages of power pumps.

Industrial pollution has been and continues to be a major factor causing the degradation of the environment around us, affecting the water we use, the air we breathe and the soil we live on. Among the various industries, sugar mill is one of the largest and most important agro based industries in India. Sugar factory effluent or waste water popularly called spentwash is purely of plant origin containing a large quantity of soluble organic matter and plant nutrients. It does not contain any toxic elements, but the only problem is with its very high BOD, COD, electrical conductivity and colour. Hence, the spentwash management in the sugar factories and distilleries has always been a complex problem.

Chopda sugar factory is the largest industry among all operating industries in Chopda tehsil. However, this industry is seeking to increase government's revenue and employment opportunities the rampant discharge of untreated effluents causing severe environmental degradation. The present investigation has been carried out to assess the physico-chemical characteristics of effluent from Chopda sugar factory. From the result of physico-chemical

analysis of effluent of Chopda sugar factory it has been concluded that it does not always maintain BIS for industrial effluent as well as the surface water quality standard. Discharges of effluent and its percolation in adjoining field may affect the water quality of open or bore wells and the same water is being used to irrigate the crop fields may leading to deterioration of soil.

In Uttar Pradesh of India, Ajamal and Khan (1983) evaluated the physico-chemical properties of effluents of Kisan Sahkari Chini Mills Limited Satha (KSCML), Aligarh and Panniji Sugar and General Mills (PSGM), Bulandshahr and reported that the effluents of KSCML and PSGM were high in various solids, COD, BOD, chlorides, sulphates, and had low dissolved oxygen and moderately alkaline pH.

Somewhat resembling estimated values of physico-chemical parameters were reported by Roy et al (2007) who analyzed the sugar factory effluent that had high TDS (422-608 mg/L), COD (1152-17680 mg/L) and BOD(380-650 mg/L). Similarly, Siddiqui and Waseem (2012) reported high contents of COD, BOD, TSS, TDS, and low contents of DO in effluent samples collected from Sir Shadi sugar mill Ltd. Shamli in Muzaffarnager district of Western Utter Pradesh in India during 2011-12. Doke *et al* (2011) assessed physico-chemical parameters of treated waste water effluents from a sugar industry and reported low pH (4.35), total dissolved solids, (TDS, 720 mg/L) and chemical oxygen demand, (COD, 1330 mg/L) and indicated the high inorganic and organic content with an acidic load.

In another study conducted by Saranraj and Stella (2012 and 2014), physico- chemical characteristics of the collected sugar mill effluent was analyzed and they reported that the sugar mill effluent was acidic nature with brown colour and emitted unpleasant smell. The temperature of collected sugar mill effluent was 33°C and the EC was 2.58 S.m^{-1}. The TSS and TDS present in collected sugar mill effluent were 479 and 1540 mg/L respectively. It also showed high value of BOD (1090 mg/L) and COD (3260 mg/L). High amount of calcium (393 mg/L), magnesium (299 mg/L), chloride (377 mg/L), sodium (106 mg/L), potassium (125 mg/L), sulphate (430 mg/L), nitrogen (1300 mg/L), phosphorous (6.17 mg/L) and presence of traces of heavy metals (Fe^{2+} 17.0 mg/ L, Zn^{2+}- 0.79 mg/L, Pb^{2+}- 0.52 mg/L, Cu^{2+}- 0.346 mg/L and Mn^{2+}- 0.095 mg/L) were recorded in the collected sugar mill effluent sample. Most of the estimated values of various parameters were higher than the values obtained in the present investigation.

The results of study conducted by Jadhav *et al* (2013) showed that the effluents in general exceeded the limits specified in CPCB with reference to parameters such as BOD, COD, Oil and greases, total suspended solids.

4.4 CONCLUSION

In the present investigation, higher BOD and COD values of Chopda sugar factory might attributed to the spillage of molasses and lost or leaked sugar contents on the floor of the factory that are swept or washed away to be mixed within effluents causing higher levels of BOD and COD.

The effluent level found through the analysis could be reduced if suggested recommended measures were worked upon. There is a scope of recycling and reuse of water in sugar factories thereby minimizing water consumption and ultimately effluent quantity. The recycling and reuse of hot condensate water can reduce the water consumption to as low as. 100-200 litres, as against 1,500-2,000 litres per tonne of cane crushed. Proper housekeeping, periodic checking and maintenance of pipe joints, valves and glands further reduces the water consumption and effluent quantity. The effluents from the sugar factory can be treated by anaerobic biological processes (oxidation ponds and biomethanation) or by aerobic processes (aerated lagoons, activated sludge process). Anaerobic processes are easier to control and operate, produce a lower quantity of sludge and their costs are lower. Anaerobic processes decompose the organic compounds in an atmosphere free of oxygen and consequently require significantly less energy as compared to aerobic processes.

Double Sulphitation Process, already adopted by most of the sugar industries, reduces the quantity of lime sludge and press mud to a great extent. The lime sludge is usually dumped in low lying areas, whereas press mud is sold to farmers as it can be used as manure. Bagasse is either used as fuel or sold to pulp and paper industry which use them as raw materials. Molasses produced in sugar industry is raw materials for fermentation industries.

The present study reveals that a sugar factory requires only around 180 litre of water per tonne of cane as against the stipulated limit of 1,000 litres, if the condensate water is properly utilised and cooling water is recycled.

Suggestions for Water Pollution Minimization Option

a) Monitoring and Maintenance

➢ Prevention or minimization of spills and leaks through regularly inspecting and repairing various units (pumps, conveyors, pipes, and etc) and handling and storing molasses properly.

➢ Sugar factories have no flow meters installed at the inlet and outlet of each unit operation of mill and process houses to gauge water consumption or wastewater genera tion. Installation of flow meters is useful to maintain water consumption and subsequent wastewater discharge ratios. It was also observed that the in-house plant control measures or good housekeeping practices to minimize the higher levels of pollution were lacking in Chopda sugar factory. Monitoring of quantity and quality of incoming and outgoing water at the factory with flow meters by measuring the flow.

b) Process Modifications

➢ Minor changes in the sugar production and waste handling process can produce substantial reductions in wastewater volume and pollutant load.

➢ Sugar factories should be operated at optimum capacity and with minimum stoppages because raw water consumption per ton of cane crushed increases when crushing lower than the optimum capacity and when hot water production is suspended during halts in operations (cleaning, restocking, and breakdowns).

➢ For maximum sugar sucrose recovery, condensate hot water should be used for imbibitions.   For optimum recovery, imbibitions water should be maintained around 25-30% of cane used.

➢ The suspended solid level of the wastewater is much less when the sugar cane is manually harvested.

➢ Water conservation and sugar recovery can be improved by avoidance of overloading evaporators and vacuum pans, boiling at excessive rates, or operating at incorrect liquid levels

➢ Dirt and large particles in effluents can be minimized by allowing suspended particles in filter cloth washings to settle in a holding tank before being mixed with other effluents and screening wastewater before emitting to remove refuse, dirt, and remnants of the cane.

➢ Caustic wastes from the cleaning equipment should be separated from the rest of the wastewater and gradually released into furrows and blended with the other effluents.

➢ The recycling of water is the primary factor in reducing wastewater volume.

➢ Effluents from sugar mills are often used for irrigation and this is considered an apt measure if the wastes are first treated to remove oil and suspended particles and to correct the pH value.

Suggestions for cleaner environment around sugar factory:

➢ It is necessary to strengthen research and development activities in the Chopda Sugar Factory with the aim to reduce, reuse and recycle water. Reuse of water and less consumption of water reduces discharge and generation of waste water.

➢ Chopda Sugar Factory should have the pretreatment process within the plant boundary and thus waste generated from the plant can treat to reduce the level of BOD, COD, TDS, Chlorides, $Ca^{2+,}$ Mg^{2+}, PO_4^{3-}, NO_3, etc.

➢ Chopda Sugar Factory should periodically analyze the physico-chemical properties of well water and soil to know effect of effluent on these abiotic factors

➢ Most of the sugar factories don't comply with the standards set by the government and BIS for industrial wastewaters and hence most sugar factories are a major source of pollution. Existing laws of pollution control must be more stringent.

➢ The awareness program is to be initiated by the NGO's and the MPCB to discourage the investors to invest in polluting technology.