ANALYSIS OF EFFLUENT WATER FROM SEA FOOD INDUSTRIES IN KOCHI

PROJECT REPORT SUBMITTED TO MAHATMA GANDHI UNIVERSITY FOR THE PARTIAL FULFILLMENT OF THE AWARD OF THE DEGREE OF SCIENCE IN CHEMISTRY

BY
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VI SEMESTER
REG NO: 170021025623
JUNE 2020

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CERTIFICATE

This is to certify that the project entitled **"ANALYSIS OF EFFLUENT WATER FROM SEAFOOD INDUSTRIES IN KOCHI"** was carried out by **SREERENGINI NANDAKUMAR** under my supervision and guidance. The work presented here has not been reported for any other degree or diploma.

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Date: 11/6/2020

DECLARATION

I hereby declare that this project entitled **"ANALYSIS OF EFFLUENT WATER FROM SEA FOOD INDUSTRIES IN KOCHI"** is a record of bonafide work carried out during my course of study under the guidance of **Dr. V. Sivanandan Achari**, Professor and Director of School of Environmental Studies, Cochin University of Science and Technology, Kochi and Dr. SINDHU JOSEPH, Department of chemistry, Bharata Mata College, Thrikkakara.

SREERENGINI NANDAKUMAR

Place: Thrikkakara
Date: 11/6/2020

ACKNOWLEDGEMENT

First and foremost I thank God for his immense blessings which helped in the successful completion of this project.

I owe a depth of gratitude to Prof. Dr. V. Sivanandan Achari, Director, School of Environmental Studies, Cochin University of Science and Technology, for permitting me to use their laboratory and instrumentation facilities and also for his excellent guidance, constant attention, critical suggestions and personal encouragement in doing this project.

I am very grateful and thankful to my guide Dr. Sindhu Joseph, Department of chemistry, and Ms. Monisha Mohanadas, Research Scholar, School of Environmental Studies, Cochin University of Science and Technology, who gave me a chance to work under them and also inspired me a lot, providing necessary facilities in completing this project and providing support, care and valuable suggestions.

I am indebted to the faculties of Department of Chemistry, Bharata Mata College, Thrikkakara. I extend my gratitude to my classmates and my family members for their valuable advises, moral support and constant inspiration.

SREERENGINI NANDAKUMAR

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CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

1.1 Introduction

Water is one of the most abundant commodities in nature as four fifth of the Earth's surface is covered by water. Water is undoubtedly the most precious natural resource that exists on our planet. About 97% of the total resources are present in oceans which are too salient for any practical purposes like domestic, agriculture and industrial. Considerable amount of water are also locked up in polar ice caps and giant glaciers, rock crevices and minerals. This leaves only about 0.7% of the world's water resources available for ready use. Hence it is necessary to utilize the available water most carefully and economically. It is also the need of the hour, to develop appropriate and cheap technologies to treat the ocean water. Without water, life on the earth would be non-existent. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes and oceans. Subsequently, drinking water becomes scarcer at a very alarming rate.

The impurities or pollution in natural water is defined as the contamination or other alteration of the physical, chemical, biological properties of any water. The impurities present in natural water may be classified into three types as physical impurities, chemical impurities, and biological impurities.

Physical impurities are of two types:

1. Suspended matter
2. Colloidal impurities

Chemical impurities are two types:

1. Dissolved salts
2. Dissolved gases

Biological pollutants are two types:

1. Primary pollutants
2. Corollary pollutants

Physical impurities

Suspended matters like sand, clay, oil globes, vegetables and animal matter impart turbidity to water.

Colloidal impurities like emulsified oil, dyes, amino acids, finely divided silica, fats, ethers etc., impart color, odour and taste to water.

Chemical impurities

Dissolved salts like bicarbonate, carbonate, chloride, sulphate, nitrate, phosphate, Na, K, Ca, Mg, Fe. Dissolved salts of Mg and Ca in water cause hardness of water. Carbonate and bicarbonate of Ca, Mg, Na and K make the water alkaline.

Dissolved gases like O_2, N_2, CO_2 SO_2, and H_2S make water acidic and they accelerate the rate of corrosion.

Biological pollutants

Primary pollutants are bacteria, virus, and fungi. Corollary pollutants are weeds and algae. Biological pollutants cause diseases.

1.2 Sources of impurities in water

- Gases (O_2, CO_2 etc.,) are picked up from the atmosphere by rain water.
- Decomposition of plant and animal remains introduce organic impurities in water.

- Water takes impurities when it comes in contact with ground soil, rocks or impurities from sewage.

1.3 Seafood waste

Most seafood waste is currently processed in fish meal plants, where fish meal and fish oil are produced. Fish meal production consists in mincing, cooking, and pressing fish waste to separate the solid cake (the fish meal) from a liquid phase, which is centrifuged to obtain the fish oil. While fish meal is used as animal feed, pet food, or plant fertilizer due to its rich composition in protein and minerals, fish oil can be exploited for both food and nonfood uses according to its composition. Among food uses, the production of margarine and shortenings is the most common use of fish oil; nonfood applications include production of soap, glycerol, fertilizers, and substrates for fermentations.

Skin, scales, fins, and bones deriving from seafood waste can represent a valuable alternative to meat waste to produce collagen and gelatin, not presenting issues related to prion diseases and religious factors (kosher and halal products). Moreover, with respect to animal gelatin, seafood gelatin presents analogous functional properties, associated to an enhanced digestibility. Fish waste can also be considered a source of free amino acids, such as taurine and creatine, which are largely used for producing sport drinks, food supplements, infant formulae, and drugs. Free amino acids, in fact, present different biological activities: for example, taurine is involved in renal functionality and anti-inflammatory activity, while creatine is responsible for skeletal and muscle regeneration and contraction. Nowadays these free amino acids are mainly produced by chemical synthesis. However, the final products contain process contaminants and by-products that can have negative health effects. For these reason, a lot of research is being dedicated to the possibility of extracting these amino acids form fish flesh. In particular, raw mussels, fresh clams, and raw fish flesh are particularly rich in taurine, while herring, salmon, and cod are valuable sources of creatine.

1.4 Seafood processing wastewater characterization

Seafood-processing waste-water characteristics that raise concern include pollutant parameters,sources of process waste and types of wastes. In general, the waste-water of seafood-processing waste-water can be characterized by its physio-chemical parameters, organics, and nitrogen and phosphorus contents. Important pollutant parameters of the waste-water are five-day biochemical oxygen demand (BOD5), chemical oxygen demand (COD), total suspended solids (TSS), fats, oil and grease (FOG) and water usage. As in most industrial waste-waters, the contaminants present in seafood-processing waste-waters are an undefined mixture of substances, mostly organic in nature.

1.5 Seafood industry effluent treatment

Seafood-processing waste-water, the primary treatment processes are screening, sedimentation, flow equalization and dissolved air flotation. These unit operations will generally remove up to 85 per cent of the total suspended solids and 65 per cent of the BOD5 and COD per cent in the waste-water. To complete the treatment of the seafood-processing waste-waters, the waste stream must be further processed by biological treatment. Biological treatment involves the use of micro-organisms to remove dissolved nutrients from a discharge. Organic and nitrogenous compounds in the discharge can serve as nutrients for rapid microbial growth under aerobic, anaerobic or facultative conditions.

Primary treatment

- Screening - Involves removal of coarse particles like shells, flesh, skin, head etc.
- Coagulation -suspended colloidal particle removal with pH correction
- Sedimentation - large particles settle at the bottom of the tank from where they can be removed.

Secondary treatment

- Aerobic treatment- Aerobic processes such as activated sludge, lagoons, trickling filter and rotating biological contactor are suitable for organics removal.

- Anaerobic treatment- sludge degradation which produces gas and water.

Tertiary treatment

- Filtration
- Disinfection

1.6 Effects of untreated effluents releasing from seafood industries

- If the fish waste is deposited in water bodies then it leads to lowering of oxygen levels in the water due to activities of the aerobic bacteria on the organic matter.
- Causes bad odours and severe contaminations in both soil and groundwater.
- The dissolved salts promote algal growth and affect the availability of high-quality water.
- Fish by-products are, in most cases, either incorporated into animal feed or biofuels, i.e., low added-value products, or incinerated and discarded, thus increasing the energy consumption, financial cost, and environmental impact of their management processes.

1.7 Importance of seafood effluent characterization

- Sea food industry is fastly emerging to be one of the largest industries in export sector.
- Due to improper treatment the BOD and COD levels of water are increasing which owe to the rise in level of organic matter in water.
- Quantification of effluent characteristics is necessary to estimate the environmental disruption caused.

- To device an appropriate treatment technique and to test its efficiency.

1.8 Wastewater characteristics

1.8.1 pH

It refers to the acid or alkaline condition of water.

1.8.2 CONDUCTIVITY

It is a measure of the capability of water to pass electrical flow, mainly due to the presence of ions in water.

1.8.3 RESITIVITY

It is the ability of dissolved ions in water to resist electric current.

1.8.4 SALINITY

It is the saltiness or dissolved inorganic salt content of water.

1.8.5 TOTAL HARDNESS

It is the amount of calcium and magnesium in water.

1.8.6 DISSOLVED OXYGEN-DO

Amount of gaseous oxygen dissolved in an aqueous solution.

1.8.7 BIOLOGICAL OXYGEN DEMAND-BOD

It is the measure of oxygen used by microorganisms in aerobic oxidation.

1.8.8 CHEMICAL OXYGEN DEMAND

Amount of oxygen used for oxidation of organic and inorganic matter in water.

1.8.9 TOTAL SUSPENDED SOLIDS-TSS It is the dry weight of suspended particles that are not dissolved in a sample of water and can be trapped by a filter paper.

1.8.10 TOTAL DISSOLVED SOLIDS-TDS

It represents the total concentration of dissolved substances in water. Common inorganic dissolved salts are calcium, nitrates, bicarbonate etc.

1.8.11 SULPHATE

They are combination of sulfur and oxygen that are a part of naturally occurring minerals in some soil and rock formations that contain ground water. These minerals over a long time, dissolves and are released into ground water.

1.8.12 PHOSPHATE

Phosphorous present in wastewater are organic compounds, orthophosphates and polyphosphates and are water soluble.

1.9 Objectives of the study

- To study the extend of pollution created by seafood industries.
- Characterization of the sea food industrial effluents generated at each industry by physical, chemical & biological parameters.
- Efficiency of treatment plants by comparing their influents & effluents.

1.10 Literature review

YEAR	AUTHOR	MAIN CONTENT	WORK
2016	Sherly Thomas	Nano Dispersion and Flocculation System & Aerobic Treatment System are suitable for treatment of seafood processing waste water.SBSBR may be used as treatment process for nitrogen and COD removal to meet discharge requirement in seafood industry.	Status, Characterization and Treatment using Stringed Bed Suspended Bioreactor.
2010	Pankaj Chowdhury,T Viraraghavan, A Srinivasan	Anaerobic processes such as upflow anaerobic sludge blanket reactor, anaerobic filter and anaerobic fluidized bed reactor can achieve high organic removal and produce blogas. Aerobic processes such as activated sludge, rotating biological contactor, trickling filter and lagoons are done for organic removal. Anaerobic digestion followed by an aerobic process is an optimal process option for fish processing waste water treatment.	Biological treatment processes for fish processing waste water.
2006	O Lefebvre, R Moletta	Saline effluents are conventionally treated through physio-chemical means, as biological treatment is strongly inhibited by salts (mainly NaCl).Biological treatment of carbonaceous, nitrogenous andphosphorous pollution has proved to be feasible at high salt concentrations, the performance obtained depends on a proper adaptation of the biomass or the use of halophilic organisms.	Treatment of organic pollution in industrial saline waste water.
2004	Islam M.S. Khan & Tanaka M.	Shell obtained from diverse sources are subjected to washing and drying followed by crushing into powder, the chemical extraction methods include deproteination, demineralization and discoloration.	Waste loading in shrimp and fish processing effluents.

CHAPTER II

MATERIALS & METHODS USED

2.1 Sampling

This study envisages the characterization of seafood industrial effluents through organic and inorganic analysis. It was decided to select three seafood industries randomly and collected their influents and effluents. Samples were collected in a 3L plastic containers rinsed with deionized water and kept in a refrigerator. The collected samples were designated as $\mathbf{A_I}$ (influent of station A), $\mathbf{A_E}$ (effluent of station A), $\mathbf{B_I}$ (influent of station B), $\mathbf{B_E}$ (effluent of station B), $\mathbf{C_I}$ (influent of station C), $\mathbf{C_E}$ (effluent of station C).It is then analyzed for **pH, Conductivity, Resistivity, Salinity, Total hardness, DO, BOD, COD, Total Suspended Solids, Total Dissolved Solids, Sulphate, Phosphate.** These parameters were analyzed in accordance with the procedures American Public Association, APHA (1995).

2.2 Materials & Methods

2.2.1 pH

pH or potential for hydrogen is a scale used to specify how acidic or basic (or alkaline) a water-based solution is. Acidic solutions have a lower pH, while basic solutions have a higher pH. At room temperature (25°C or 77°F), pure water is neither acidic nor basic and has a pH of 7.

The pH scale is logarithmic and inversely indicates the concentration of hydrogen ions in the solution (a lower pH indicates a higher concentration of hydrogen ions). This is because the formula used to calculate pH approximates the negative of the base 10 logarithm of the molar concentration[a] of hydrogen ions in the solution. More precisely, pH is the negative of the base 10 logarithm of the activity of the hydrogen ion.

At 25 °C, solutions with a pH less than 7 are acidic, and solutions with a pH greater than 7 are basic. The neutral value of the pH depends on the temperature, being lower than 7 if the temperature increases. The pH value can be less than 0 for very strong acids, or greater than 14 for very strong bases.

$$\mathbf{pH = - \log [H_3O^+]} \qquad \mathbf{(1)}$$

pH was measured by using multiparameter.

2.2.2 CONDUCTIVITY

Conductivity (k) is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Principle

Conductance, G, is defined as the reciprocal of resistance, R: **G= 1/R** where the unit of R is ohm and G is ohm? (Sometimes written mho). Conductance of a solution is measured between two spatially fixed and chemically inert electrodes.

To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal. The conductance of a solution, G, is directly proportional to the electrode surface area, A, cm", and inversely proportional to the distance between the electrodes, L, cm. The constant of proportionality, k, such that: **G=K (A/L)** **(2)**is called "conductivity" (preferred to "specific conductance"). It is a characteristic property of the solution between the electrodes. The units of k are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micro mhos per centimeter (umho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the Siemens (S) and conductivity is reported as milli-Siemens per meter (mS/m); 1 mS/m = 10 umhos/cm and 1 uS/cm = 1 umho/cm. To report results in SI units

of mS/m divide umhos/cm by 10.Conductivity was measured by using multiparameter.

2.2.3 RESISTIVITY

Resistivity is the reciprocal of conductivity and either may be used to inexpensively monitor the ionic purity of water. Resistivity or conductivity of water is a measure of the ability of the water to resist or conduct an electric current. The ability of water to resist or conduct an electric current is directly related to the amount of ionic material (salts) dissolved in the water. Dissolved ionic material is commonly referred to as total dissolved solids or TDS. Water with a relatively high TDS will have a low resistivity and a high conductivity. The opposite is true for water with low TDS.

The standard for monitoring the purity of water by electrical resistance is termed specific resistance corrected to 25°C or R-25. The resistivity of absolute pure water is 18.2 (rounded) M2 x cm at 25°C or 0.055 micro-Siemens /cm. This only accounts for the dissolved ionic impurities commonly found in water.

Water Resistivity = R/ (1/A), **(3)**

Where, R is the measured resistance across the cell, A is the cross-sectional area of each electrode, 1 is the gap separating the electrodes. Resistivity was measured by using multiparameter.

2.2.4 SALINITY

Salinity is an important unit less property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. Salinity is either expressed in grams of salt per kilogram of water, or in parts per thousand (ppt, or %). Seawater is on average 35 ppt, but it can range between 30 - 40 ppt. This variation occurs because of differences in evaporation, precipitation, freezing, and freshwater runoff from land at different latitudes and locations. Seawater salinity also varies by water depth because water density and pressure increases with depth.

Water with salinity above 50 ppt is brine water, though not many organisms can survive in such a high salt concentration.

Salinity can be determined using the relationship,

Salinity (ppt) = 0.00180665 C1 (mg/L) (4)

This is based on the assumption that most of the ions in the solution are non carbonate salt ions (e.g., Na+, K+, or C1), and converts the conductivity reading to a salinity value.

Salinity was determined by argentometric method.

Reagents

a) Potassium dichromate indicator solution

Dissolve 5.0g K_2CrO_4 in a little distilled water. Add $AgNO_3$ solution until a definite red precipitate was formed. Let stand for some time, filtered and diluted to 1L.

b) Standard $AgNO_3$ solution(0.0141N)

Accurately weigh 2.395g of $AgNO_3$ and dissolve in distilled water and diluted to 1L, then standardize against 0.0141N NaCl.

c) Standard NaCl solution (0.0141N)

Accurately weigh 0.824g NaCl dried at 140˚C and diluted in chloride free water to 1L

Procedure

a) Standardization of $AgNO_3$

Pipette out 20mL of NaCl solution to a 250mL conical flask and add 1mL of K_2CrO_4 indicator solution and titrate against $AgNO_3$ solution taken in the burette. When the solution turns yellow to reddish orange is the end point.

b) Determination of Chloride

Measure50mL water sample and filtrate the sample in the pH range 7-10 directly. Add 1mL K_2CrO_4 in the sample and titrate against $AgNO_3$ solution taken the burette. Appearance of pinkish yellow colour is the end point.

2.2.5 TOTAL HARDNESS

Aim

To determine the Total hardness of given water sample by EDTA by titrimetric method.

Principle

Ethylene Diamine Tetra Acetic acid and its sodium salts (EDTA) from a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Erichrome Black T (EBT) is added to aqueous solution containing calcium ions and magnesium ions at a pH of 10, the solutions become wine red. If EDTA is added as a titrant, the calcium and magnesium has been complexed, solution turn from wine red to blue making the end point of titration. Mg^{2+} must be present to yield a satisfactory end point. To ensure this, a small amount of complex metrically neutral magnesium salt of EDTA is added to buffer.

Ca^{2+} + Mg^{2+} + EBT→ Ca-EBT + Mg-EBT (wine red complex)

Ca-EBT + Mg-EBT + EDTA → Ca-EDTA + Mg-EDTA + EBT (blue)

From the titre value, hardness of water can be calculated using the formula.

$$\textbf{Total hardness} = \frac{V_{EDTA} \times M_{EDTA} \times 100 \times 1000}{\text{Volume of sample used}} \qquad (6)$$

The sharpness of end point increases with increasing pH however pH can't be increased indefinitely because of danger of precipitate $CaCO_3$/$Mg(OH)_2$ and because the dye changes the colour at high pH value. The specific pH of 10.0 + 0.1 is a satisfactory compromise. A limit of 5 minute is set for the duration of the titration to minimize the tendency towards calcium carbonate precipitation.

Reagents

- EDTA solution (Molecular weight = 372.25):

EDTA solution is prepared by dissolving 3.772g of AR disodium dihydrogen phosphate in tetra acetic acid in one liter (0.1 mg of $MgCl_2 6H_2O$ is added while dissolving EDTA)

- Buffer solution:

NH_4Cl- NH_4OH buffer solution of pH 10 is prepared by mixing 6.75 g of NH_4Cl and 57 ml of conc.NH_3 solution. It is made upto 100 ml.

- Eriochrome Black T indicator:

0.4 % solution of the dye stuff in methanol may be prepared.

Procedure

1 g of $CaCO_3$ is dissolved in a little dil.HCl till no more effervescence is observed and diluted to one litre and stored as a clear solution. 1 mg of solution is equivalent 1mg of $CaCO_3$.

Standardization of EDTA solution

20 ml of standard $CaCO_3$ solution is pipette out into a conical flask and 2 ml of solution and 4 drops of Erichrome Black T are added and titrated against EDTA from burette. At the end point, the colour changes from wine red to blue.

Estimation of total hardness of water sample

50 ml of water sample is taken in a conical flask. 2 ml of buffer solution and 4 drops of Erichrome Black T indicator are added. The solution is then titrated against EDTA solution from the burette until the colour changes from wine red to blue at the end point. **N:B**

- The presence of Mg is a must for sharp colour change at the end point with Erichrome Black T indicator. So if no magnesium ion is present the water sample, it is necessary to add 0.1 ml magnesium EDTA solution (0.1) before adding the indicator.

- The pH should be maintained at 10, since the indicator give red colour ions below pH 6 and orange above pH 6.

2.2.6DISSOLVED OXYGEN (DO)

Dissolved oxygen (DO) is a measure of how much oxygen is dissolved in the water - the amount of oxygen available to living aquatic organisms. Owing to the organic load of wastewater, discharged effluents from wastewater treatment facilities usually contribute to oxygen demand level of the receiving water. There is increased depletion of dissolved oxygen (DO) in surface water that receives ill-treated wastewater. Water solubility of oxygen at 523.15K and pressure = 1 bar is at 40 mg/L water. In air with a normal composition the oxygen partial pressure is 0.2 atm. This results in **dissolution of 40 x 0.2 = 8 mg 02/L in water that comes in contact with air, i.e., dissolved oxygen**.

Aim

To determine the Dissolved Oxygen of the given sample.

Reagents

WinklerA, WinklerB, conc.sulphuric acid, 0.025M sodium thiosulphate, starch solution.

Procedure

A known amount of sample is diluted with dilution water (aerated water) and closed immediately which is taken in 300mL BOD bottles. After incubation 1 mL of WinklerA (480gm of $MnSO_4$ in one L) and 1mL of Winkler B (alkaline KI solution -500g KOH and 10g KI in 1L) are added. A brownish orange flock appears. When the flock settles to the bottom, 1mL of conc.sulphuric acid is added, stopped and inverted several times to dissolve the floc Titrate 50mL of sample with 0.025M sodium thiosulphate to a pale straw coloured and then 2mL of starch solution was added and a blue colour was formed. Titration was continued until the sample turned colourless.

$$\textbf{DO (mg/L)} = \frac{\textbf{8 X V}_{\textbf{Titrant}}\textbf{ X N}_{\textbf{Titrant}}\textbf{ X 1000}}{\textbf{Volume of the sample}} \qquad \textbf{(7)}$$

2.2.6 BIOLOGICAL OXYGEN DEMAND (BOD)

Aim

To determine the Biological Oxygen Demand (BOD) of the given sample.

Reagents

WinklerA, WinklerB, conc.sulphuric acid, 0.025M sodium thiosulphate, starch solution.

Procedure

A known amount of sample is diluted with dilution water (aerated water) and closed immediately which is taken in 300mL BOD bottles. Two such bottles are taken. One bottle is used for the determination of initial DO and other was incubated for 3 days. After incubation 1 mL of WinklerA (480gm of $MnSO_4$ in one L) and 1mL of Winkler B (alkaline KI solution -500g KOH and 10g KI in 1L) are added. A brownish orange flock appears. When the flock settles to the bottom, 1mL of conc.sulphuric acid is added, stopped and inverted several times to dissolve the floc Titrate 50mL of sample with 0.025M sodium thiosulphate to a pale straw coloured and then 2mL of starch solution was added and a blue colour was formed. Titration was continued until the sample turned colourless. Initial and final DO content in the sample was thus determined.

$$\textbf{BOD} = \frac{\textbf{Initial DO} - \textbf{Final DO}}{\textbf{P}} \qquad \textbf{(8)}$$

Where P = dilution factor

$$P = V_{\text{Sample}} (V_{\text{Sample}} + V_{\text{Dilution factor}})$$

2.2.7 CHEMICAL OXYGEN DEMAND (COD)

AIM

To determine the Chemical Oxygen Demand (COD) of the given sample.

APPARATUS

A. Reflux apparatus consisting of 500 or 250 mL Erlenmeyer flasks with ground-glass 24/40 neck and 300-mm jacket lievig, west, or equalent condenser with 24/40 ground-glass joint, and a hot plate having sufficient power to produce at least 1.4W/cm2 of heating surface or equivalent.

B. Blender.

C .Pipets, class A and wide-bore.

REAGANTS

a. Standard potassium dichromate solution, 0.04167M:

Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, in distilled water and dilute to 1000 mL. This reagent undergoes a six-electron reduction reaction; the equivalent concentration is 6 × 0.04167M or 0.2500N.

b. Sulfuric acid reagent:

Add Ag_2SO_4, reagent or technical grade, crystals or powder, to conc. H_2SO_4 at, the rate of 5.5 g Ag_2SO_4/Kg H_2SO_4. Let stand 1 to 2 to dissolve, Mix.

c. Ferroin indicator solution:

Dissolve 1.485 g 1, 10-phenanthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute 10 to 100 mL. This indicator solution may be purchased already prepared.*

d. Standard ferrous ammonium sulfate (FAS) titrant, approximately 0.25M:

Dissolve 98g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 mL conc. H_2SO_4, cool, and dilute to 1000 mL.

Standardize this solution daily against standard $K_2Cr_2O_7$ solution as follows:

e. Standard potassium dichromate solution, 0.04167M:

Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, in distilled water and dilute to 1000 mL. This reagent undergoes a six-electron reduction reaction; the equivalent concentration is 6 × 0.04167M or 0.2500N.

f. Sulfuric acid reagent:

Add Ag_2SO_4, reagent or technical grade, crystals or powder, to conc. H_2SO_4 at, the rate of 5.5 g Ag_2SO_4/Kg H_2SO_4. Let stand 1 to 2 to dissolve, Mix.

g. Ferroin indicator solution:

Dissolve 1.485 g 1, 10-phenanthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute 10 to 100 mL. This indicator solution may be purchased already prepared.*

h. Standard ferrous ammonium sulfate (FAS) titrant, approximately 0.25M:

Dissolve 98g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 mL conc. H_2SO_4, cool, and dilute to 1000 mL.

Standardize this solution daily against standard $K_2Cr_2O_7$ solution as follows:

Dilute 25.00 mL standard $K_2Cr_2O_7$ to about 100 mL. Add 30 mL conc.H_2SO_4 and cool. Titrate with FAS titrant using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator.

Molarity of FAS solution

$$= \text{Vol. of 0.04167M } K_2Cr_2O_7 \text{ solution titrated, mL} \quad X \quad 0.2500$$
$$\text{Volume of FAS used in titration, mL}$$

(9)

i. Mercuric sulfate, $HgSO_4$, crystals or powder.

j. Sulfamic acid:

Required only if the interference of nitrites is to be eliminated (see 5220A.2 above).

k. Potassium hydrogen phthalate (KHP) standard, $HOOCC_6H_4COOK$:

Lightly crush and then dry KHP to constant weight at 110°C. Dissolve 425 mg in distilled water and dilute to 1000 mL. KHP has a theoretical COD of 1.176 mg O_2/mg and this solution has a theoretical COD of 500 μg O_2/mL. This solution is stable when refrigerated, but not indefinitely. Be alert to development of visible biological growth. If practical, prepare and transfer solution under sterile conditions. Weekly preparation usually is satisfactory.

Procedure

A. Treatment of samples with COD of > 50 mg O_2/L:

Blend sample if necessary and pipet 50 mL into a 500 mL refluxing flask. For samples with a COD of > 900mg O_2/L, use a smaller portion diluted to 50 mL. Add 1g $HgSO_4$, several glass beads, and very slowly add 5.0 mL sulfuric acid reagent, with mixing to dissolve $HgSO_4$. Cool while mixing to avoid possible loss of volatile materials. Add 25 mL 0.04167M $K_2Cr_2O_7$ solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70mL) through open end of condenser. Continue swirling and mixing while adding sulfuric acid reagent.

CAUTION: Mix reflux mixture thoroughly before applying heat to prevent local heating of flask bottom and possible blow out of flask contents.

Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 hrs. Cool and wash down condenser with distilled water. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator although the quantity of ferroin indicator is not critical use the same

volume for all titrations. Take as the end point of the titration the first sharp colour change from blue-green to reddish brown that persists for one minute or longer. Duplicate determinations should agree within 5 percentage of their average. Samples with suspended solids or components that are slow to oxidize may require additional determinations. The blue-green may reappear. In the same manner, reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of sample.

B. Alternate procedure for low-COD samples: follow procedure of A, with 2 exceptions:

(i) Use standard 0.004167 M $K_2Cr_2O_7$, and

(ii) Titrate with standardized 0.025 M FAS. Exercise extreme care with this procedure because even a trace of organic matter on the glassware or from the atmosphere may cause gross errors. If a further increase in sensitivity is required, concentrate a large volume of sample before digesting under reflux as follows: Add all reagents to a sample larger than 50 mL and reduce total volume to 150 mL by boiling in the refluxing flask open to the atmosphere without the condenser attached. Compute amount of HgSO4 to be added (before concentration) on the basis of a weight ratio of 10:1, $HgSO_4$: Cl^- , using the amount of Cl^- present in the original volume of sample. Carry a blank reagent through the same procedure. This technique has the advantage of concentrating the sample without significant losses of easily digested volatile materials. Hard-to-digest volatile materials such as volatile acids are loss, but an improvement is gained over ordinary evaporative concentration methods. Duplicate determinations are not expected to be as precise as in 5220B.A.

C. Determination of standard solution:

Evaluate the technique and quality of reagents by conducting the test on a standard potassium hydrogen phthalate solution.

$$\textbf{COD (mg } O_2 \textbf{ / L)} = \frac{\textbf{8000 X M X } (V_1 - V_2)}{\textbf{Volume of sample}} \qquad \textbf{(10)}$$

Where M = molarity of FAS, V1 = volume of FAS consumed by blank
V2 = volume of FAS consumed by the sample.

2.2.6 TOTAL SUSPENDED SOLIDS (TSS)

Aim

To determine the total suspended solids of given water samples.

Principle

A well-mixed sample is filtered through a weighed standard glass - fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

$$\text{TSS} = \frac{[(\text{Weight of residue + filter paper}) - (\text{weight of filter paper alone})] \times 1000}{\text{Volume of Sample}} \quad (11)$$

Apparatus

180°C drying oven.

Procedure

Assemble the filtering apparatus. The sample is well stirred and a measured volume of sample is pipetted into the filter paper wetted by double distilled water. It is then washed with three successive 10mL of distilled water and continued suction for about 3 minutes and dry for 1 hour at 103-105˚C,cooled and weighed.

2.2.7 TOTAL DISSOLVED SOLIDS (TDS)

Total dissolved solids (TDS), is a measure of the dissolved combined content of all inorganic and organic_substances present in a liquid in molecular, ionized, or micro-granular (colloidal sol) suspended form. TDS is sometimes referred to as parts per million (ppm). Water quality levels can be tested using

a digital TDS ppm meter. Although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects), it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

Total dissolved solids equals correlation factor times conductivity or

TDS = KE ~ EC. This should give you the dissolved solids in milligrams per liter. **The correlation factor ke varies between 0.55 and 0.8.**

It was measured by using multiparameter.

2.2.8 SULPHATE

Turbidimetric Method

Reagents

- Standard sulfate solution
  Accurately weigh out 0.1479 g of anhydrous sodium sulfate and dissolve in distilled water and made up to 1000 ml in a standard flask (the solution contains 100 $MgSO_4^{2-}$)
- Buffer solution A
  Dissolve 15 g of Magnesium Chloride ($MgCl_2.6H_2O$) and 2.5 g of sodium acetate (CH_3COONa), 0.5 g of potassium nitrate and 10 ml of acetic acid (99%) in 250 ml of distilled water and made upto 500 ml
- Buffer solution B
  $BaCl_2$ Crystals of uniform size

❖ In addition to all the chemicals in buffer A add 0.111 g of anhydrous sodium sulfate. This is to be used for samples with sulfate concentration less than 10 mg/L.

Principle

Determination method is to measure the barium sulfate suspension obtained by the addition of barium chloride in acetic acid medium measured for light scattering with nephelometer.

$$SO_4^{2-} + BaCl_2 \rightarrow BaSO_4$$

Procedure

Preparation of standard curve:

From the standard sulfate solution, pipette out 10 ml, 20 ml, 30 ml, 40 ml and 50 ml solution into different 100 ml standard flask and dilute with distilled water and made up to mark. Then pipette out 20 ml of the solution into different 250 ml conical flask. Then add 4 ml buffer solution into all conical flasks. Then add a pinch of $BaCl_2$ into the solution and shake the cuvette and take readings in spectrophotometer at a wavelength of 420 nm (using glass cuvette).

Determination of sulfate in samples:

Measure 25 ml of the solution in a measuring jar and transfer into different 250 ml conical flask. Then add 5 ml buffer solution into conical flask. Then add a pinch of $BaCl_2$ into the solution and shake for 1 min. Immediately transfer the solution into a cuvette and take readings in spectrophotometer at a wavelength of 420 nm using glass cuvette.

2.2.11 PHOSPHATE

Principle

Ammonium molybdate and potassium antimonyl tartrate react in the acid medium with dilute solutions of orthophosphate to form a heteropoly acid-phosphomolybdic acid- that is reduced to intensely colored molybdenum blue by ascorbic acid. Interference: Arsenates react with the molybdate reagent to produce a blue color. Hexavalent chromium and nitrite interfere with the phosphate determination. Minimum detectable concentration is 10 µg/L.

Apparatus

Spectrophotometer with infra-red photo tube for use at 880 nm.

Instrument Used

Varian model Cary 50 c UV

Reagents

- Sulfuric acid solution (5N):
  70 mL conc. H2SO4 is diluted with distilled water to 500 mL.
- Potassium antimonyl tartrate solution:

  Dissolved 1.3751g potassium antimonyl tartrate in 400 mL distilled water taken in a 500 mL volumetric flask and diluted to the volume. Store in a glass stoppered bottle.

- Ammonium molybdate solution:

  Dissolved 20 g ammonium molybdate tetra hydrate in 500 mL distilled water and stored in a plastic bottle at 4 □C.

- Ascorbic acid (0.1M):

  1.76 g ascorbic acid is dissolved in 100 mL distilled water. This solution is stable for about one week at 4 □C.

- Combined reagent:

  50 mL of 5N H_2SO_4, 5mL potassium antimonyl tartrate solution, 15mL ammonium molybdate solution and 30 mL ascorbic acid solution are mixed together to obtain 100 mL of combined reagent. After the addition each reagent mix the solution thoroughly. If turbidity is formed in the combined reagent, stirred it and let it stand for a few minutes until turbidity disappears. The reagent is stable for 4 hours.

- Stock phosphate solution:

  Dissolved 219.5g anhydrous potassium dihydrogen phosphate, KH_2PO_4 in distilled water and diluted to 1000 mL (1mL = 50micro gram PO_4-P).

- Standard phosphate solution:

  50.0 mL stock phosphate solution is taken and diluted to 1000 mL with distilled water (1 mL= 2.50 micro gram).

Procedure

Treatment of the sample: Pipetted 50 mL of the water sample into an acid washed and oven dried 125 mL Erlenmeyer flask. Added one drop of phenolphthalein indicator and if color developed, neutralize the pH with 5N H_2SO_4. 8 mL combined reagent is added and mixed well. Measured at wavelength 880 nm, 10 minutes after colour development but not longer than 30 minutes. Use distilled water as blank with combined reagent. Now put the blank along with the samples in spectrometer for analysis.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Results

PARAMETER	A_I	A_E	B_I	B_E	C_I	C_E
pH	7.04	7.67	7.04	7.66	7.87	7.79
CONDUCTIVITY (mS)	5.61	3.36	4.239	1.207	8.427	8.76
RESITIVITY (Ω)	62.74	159.6	126.3	445.6	63.55	61.22
SALINITY (mg/L)	3604	1288.8	1650	4352	3399	3537
TOTAL HARDNESS (mg/L)	348	232	116	52	424	370
DO (mg/L)	0.39	4.62	0.02	4.66	0.17	0.39
BOD (mg/L)	1280	19.5	2580	1260	1710	129
COD (mg/L)	1682	102	3764	1834	2156	678
TSS (mg/L)	234.1	18.4	860.8	343.2	440.4	64.4
TDS (mg/L)	3794	3132	3950	1125	7855	8765
SULPHATE (mg/L)	163.58	85.62	36.32	6.36	140.12	53.88
PHOSPHATE(mg/L)	8.64	7.75	11.09	9.83	16.16	16.11

3.2 DISCUSSION

3.2.1 pH

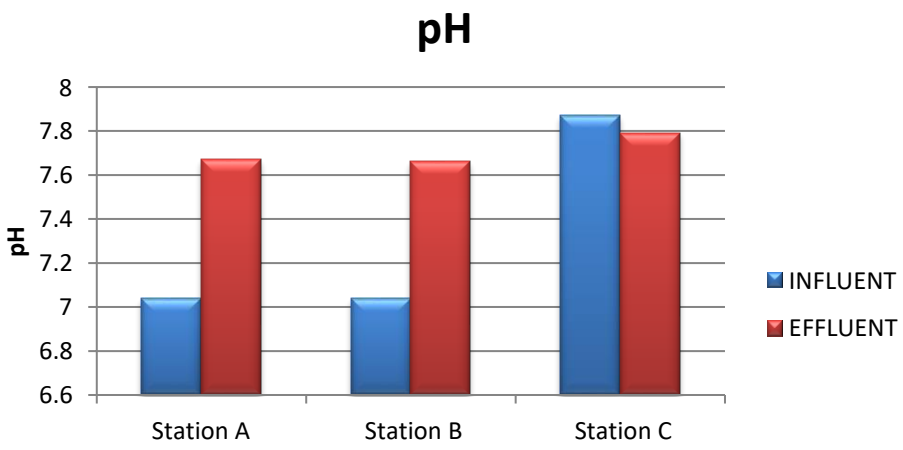

Fig 3.2.1 : Comparison of pH of influent and effluent of wastewater treatment plants

Determination of pH is an inevitable part in the wastewater treatment process. As a chemical component of water, it may reveal the contamination of wastewater or indicate the need for pH adjustments for the biological treatment of the water. The pH limit range is 6.5-8.5. The wastewater treatments are most effective at slightly alkaline pH of 7-8. Here, in case of station A, the pH is changed from 7.04 to 7.67 and in case of station B it is from 7.04 to 7.66. In both cases there is an increase in pH. But in case of station C, the pH is decreased from 7.87 to 7.79. Even though there is variation in pH before and after the treatment process, it is clear that the pH of these three industrial effluents is within the limit or close to neutral.

3.2.2 CONDUCTIVITY

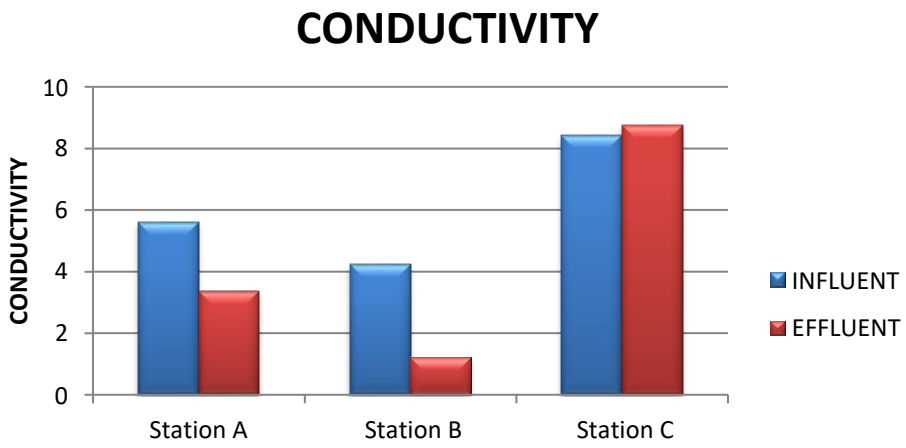

Fig 3.2.2 : Comparison of conductivity of influent and effluent of wastewater treatment plants.

Conductivity of water is its ability to conduct an electric current. Measurement of conductivity is important in wastewater treatment process, because it gives how much dissolved substances, chemicals and minerals are present in the water. Higher the amount of impurities, higher is the conductivity. Here, in case of station A and B, the conductivity decreased from 5.61mS to 3.3 mS and 4.239mS to 1.207mS respectively, while in case of station C conductivity increased from 8.427mS to 8.76mS. On comparing, one can say that among the three industries both A and B are efficient to remove the impurities to some extent.

3.2.3 RESISTIVITY

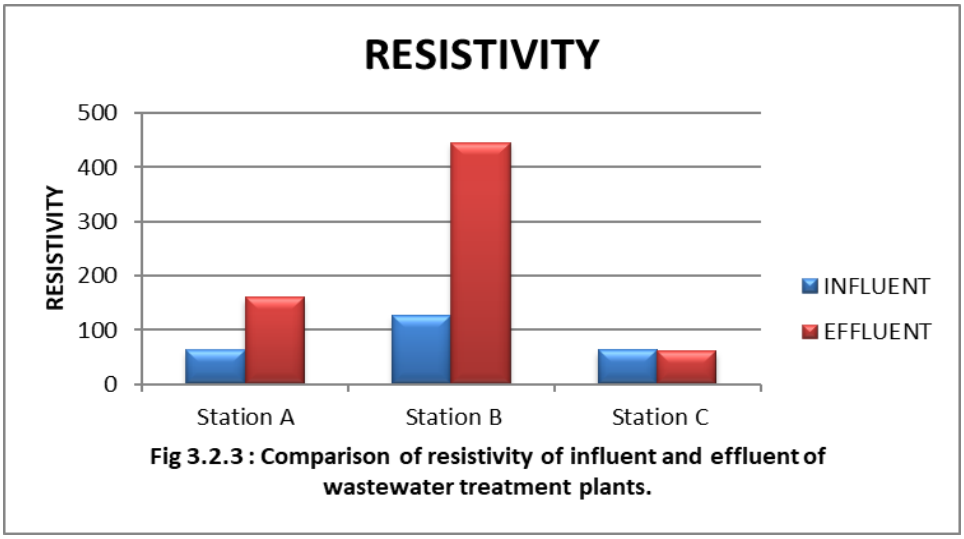

Fig 3.2.3 : Comparison of resistivity of influent and effluent of wastewater treatment plants.

Resistivity of water is its ability to resist an electric current. It is the reciprocal of conductivity and measured in ohms. Water with higher concentration of dissolved salts will have lower resistivity. Here, the resistivity is increased from 62.74Ω to 159.6Ω in case of station A, 126.3Ω to 445.6Ω in case of station B and decreased from 63.55Ω to 61.22Ω in case of station C. Since the increase in resistivity indicates lower concentration of dissolved salts, we can say that both A and B are efficient to lower the concentration of dissolved salts in the effluent while station C shows not much variation in the resistivity in the effluent.

3.2.4 SALINITY

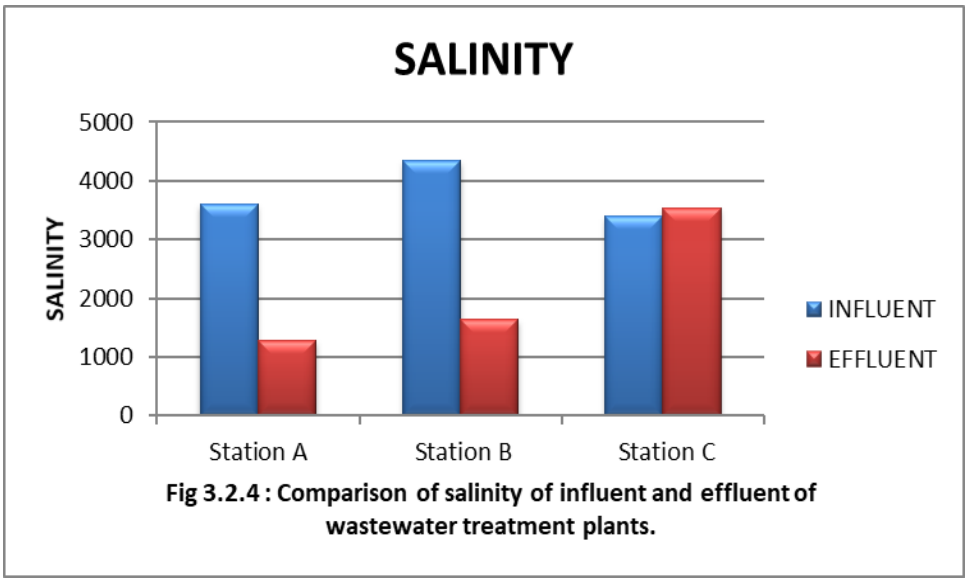

Fig 3.2.4 : Comparison of salinity of influent and effluent of wastewater treatment plants.

Salinity is the total concentration of the dissolved salts in water. Conductivity and salinity have a strong correlation. Salinity is important as it affects the dissolved oxygen solubility. The higher the salinity, the lower the DO concentration. In case of station A and station B, salinity is decreased from 3604mg/L to 1288.8mg/L and 4352mg/L to 1650mg/L respectively. But in case of station C, shows a slight increase in salinity in the effluent.

3.2.5 TOTAL HARDNESS

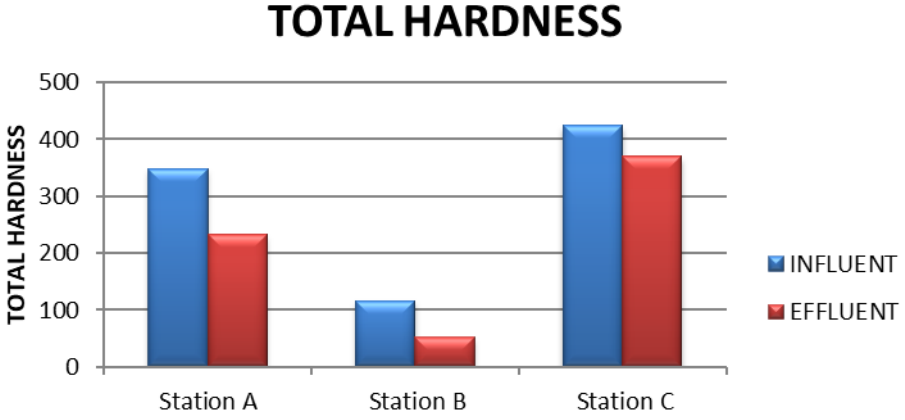

Fig 3.2.5 : Comparison of total hardness of influent and effluent of wastewater treatment plants.

Hardness is the sum of calcium and magnesium concentrations, both expressed as calcium carbonates, in mg/L. From the graph it is clear that in case of all the three industries there is a decrease in total hardness after the treatment process. In station A, it is decreased from 348mg/L to 232mg/L, in station B, from 116mg/L to 52mg/L and in station C, from 424mg/L to 370mg/L. That is, station A decreased total hardness by 33.3%, station B by 55.17% and station C by 12.73% and hence one can say, among the three stations, station B is more efficient.

3.2.6 DISSOLVED OXYGEN (DO)

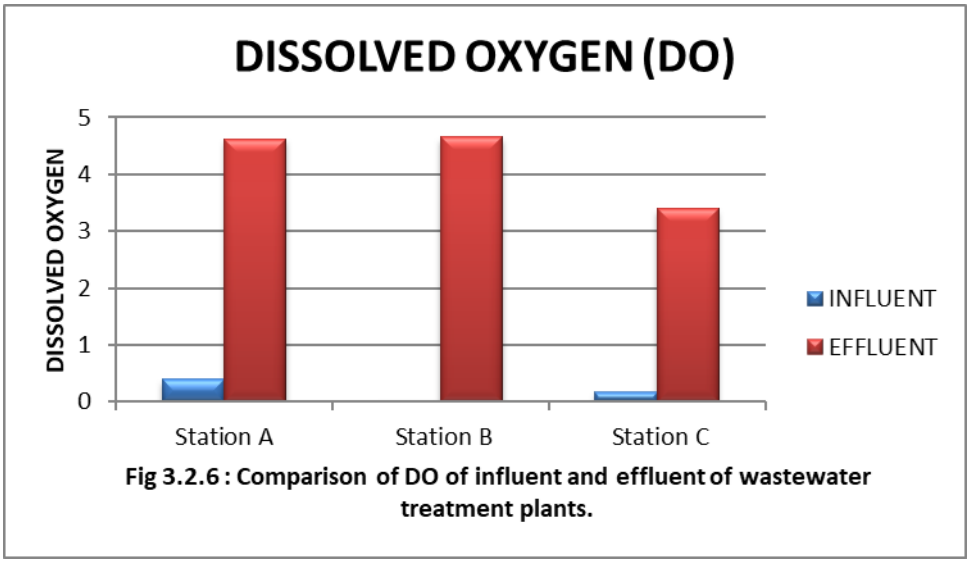

Fig 3.2.6 : Comparison of DO of influent and effluent of wastewater treatment plants.

DO is the measure of how much oxygen is dissolved in the water, the amount of oxygen available to living organisms. The amount of oxygen consumed by microorganisms to decompose the organic contents present in the waste water is called Biological Oxygen Demand (BOD). That is, DO is inversely proportional to BOD. Here, the DO level is increased from 0.39mg/L to 4.62 mg/L in station A, 0.02 mg/L to 4.66 mg/L in station B and 0.17 mg/L to 3.39 mg/L in station C. That is, all the three industries are efficient in increasing DO levels in the effluent.

3.2.7 BIOLOGICAL OXYGEN DEMAND (BOD_5)

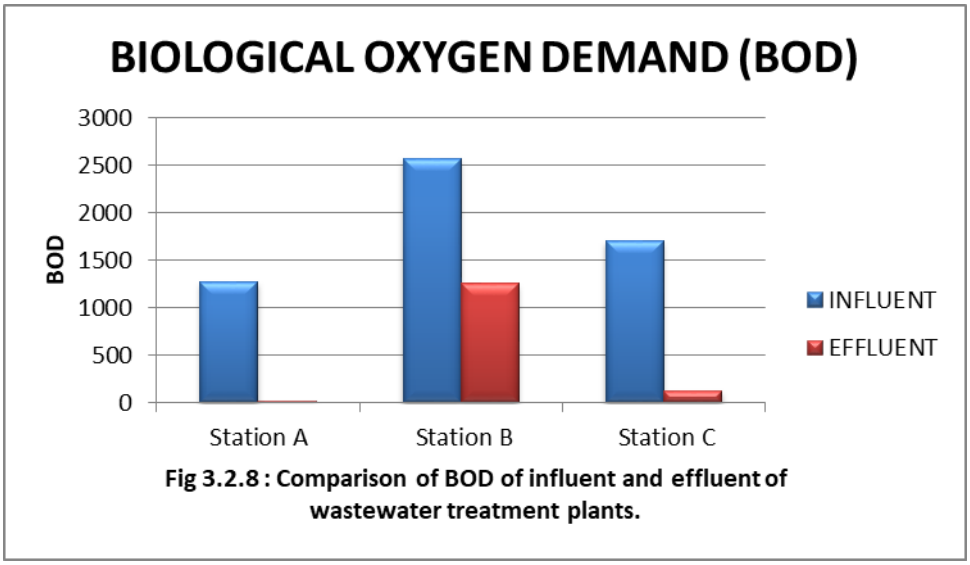

Fig 3.2.8 : Comparison of BOD of influent and effluent of wastewater treatment plants.

Biological Oxygen Demand is an important parameter because it provides an index to assess the effect of discharged seafood effluent on the environment. It is the amount of oxygen utilized by microorganisms to decompose the organic content present in the wastewater. In case of station A, the BOD_5 level decreased from 1280 mg/L to 19.5 mg/L, i.e., by 98.47%, in station B, it is decreased from 2580 mg/L to 1260 mg/L, i.e., by 51.16% and in station C, it is decreased from 1710 mg/L to 129 mg/L, i.e. 92.45%.

3.2.8 CHEMICAL OXYGEN DEMAND (COD)

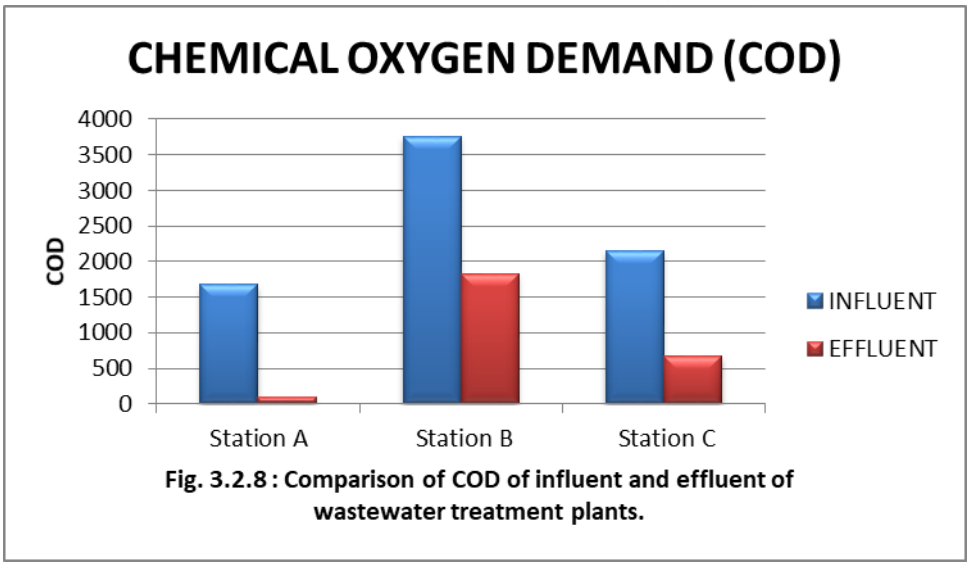

Fig. 3.2.8 : Comparison of COD of influent and effluent of wastewater treatment plants.

Chemical Oxygen Demand is the amount of oxygen used for the oxidation of organic and inorganic matter in water. COD is an important parameter because like BOD it also provides an index to assess the effect of discharge of seafood industrial effluent on the environment. Here, the COD level is decreased from 1682 mg/L to 102 mg/L, 3764 mg/L to 1834 mg/L and 2156 mg/L to 678 mg/L in stations A, B and C respectively. Station A decreased the COD level by 93.93%, station B decreased by 51.27% and station C decreased by 68.55%. i.e. among the three, station A is more efficient.

3.2.9 TOTAL SUSPENDED SOLIDS (TSS)

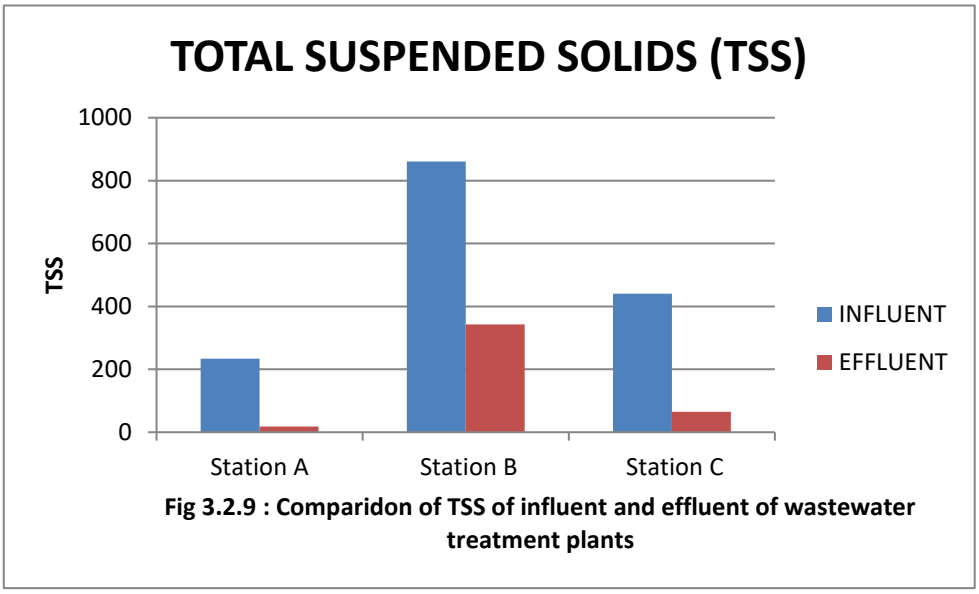

Fig 3.2.9 : Comparidon of TSS of influent and effluent of wastewater treatment plants

Total suspended solids play an important role in waste water treatment. TSS test results are routinely used to assess the performance of conventional treatment processes. In present study, the TSS in the Influent of the treatment Plant is between 234.1mg/L to 860.4 mg/L. And a considerable decrease in all the samples after treatment.

3.2.10 TOTAL DISSOLVED SOLIDS (TDS)

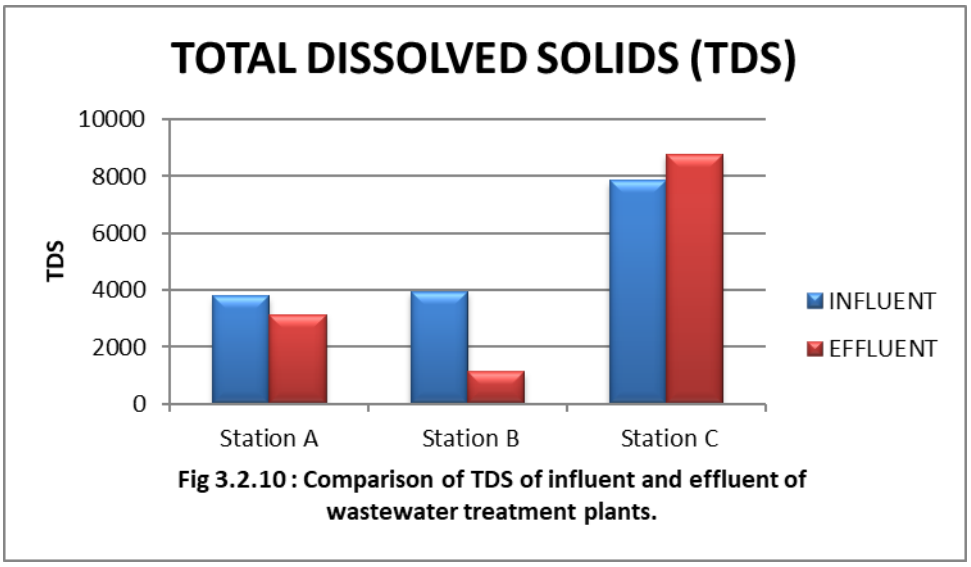

Fig 3.2.10 : Comparison of TDS of influent and effluent of wastewater treatment plants.

TDS represents the total concentration of dissolved substances in water. It is an important parameter. The extremes of TDS concentrations badly effect the growth of much aquatic life and death may occur. In case of station A and station B, there is a decrease in the TDS concentrations while in case of station C, there is a slight increase in TDS concentration.

3.2.11 SULPHATE

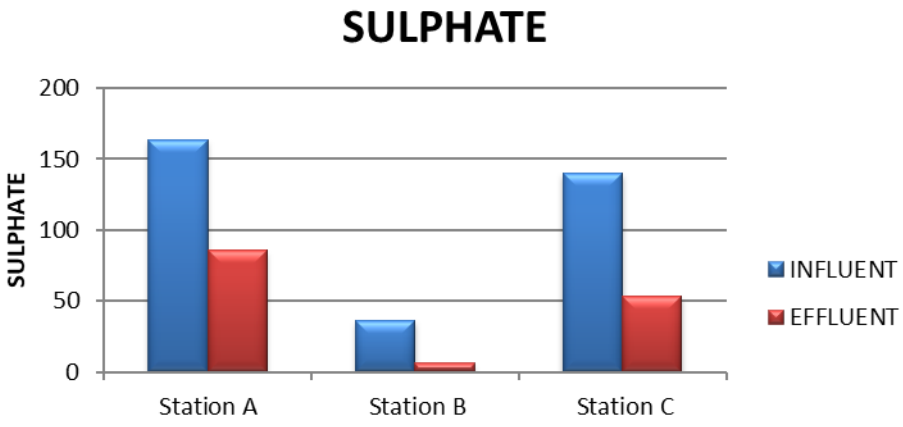

Fig 3.2.11 : Comparison of sulphate of influent and effluent of wastewater treatment plants.

Most of the seafood industrial effluents contain a high concentration of sulfate. Anaerobic treatment is widely used for the treatment of high organic content wastewater. Here the sulfate concentration is reduced after the treatment process of all the three industries. Station A decreased the sulfate concentration by 47.65%, station B by 82.48% and station C by 61.54%. i.e. station B is more efficient among the three.

3.2.12 PHOSPHATE

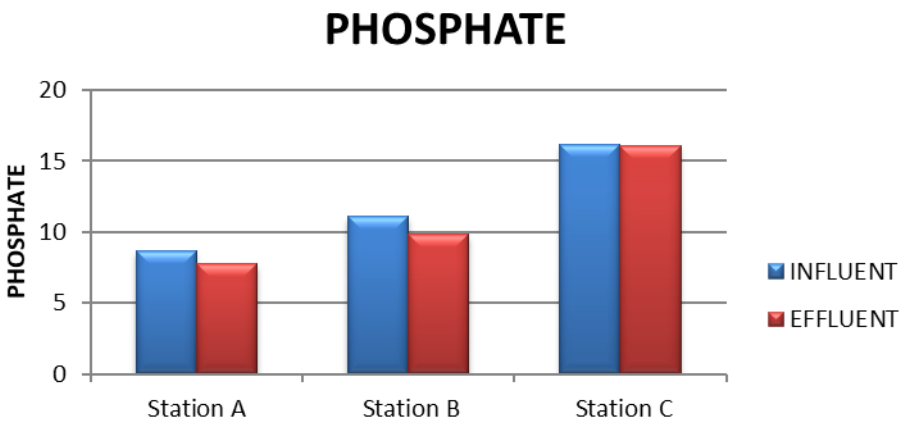

Fig 3.2.12 : Comparison of phosphate of influent and effluent of wastewater plants.

Phosphate is one of the contributing factors in the increased eutrophication of lakes and natural water bodies. Here, there is a decrease in phosphate concentration by the three industries. Station A decreased the phosphate concentration by 8.39%, station B by 10.17% and station C by 0.30%. i.e. station B is more efficient among the three.

CHAPTER IV

CONCLUSION

Seafood industry is quickly emerging to be one of the largest industries in the export sector. Even though several technologies were introduced for the management of wastewater, as time passing the percentage of waste production by the industries increasing this makes it inefficient. As a result the water bodies get polluted with organic pollutants, which is a major issue that requires immediate attention. This study makes an effort to check the efficiency of treatment plants in seafood industries in Kochi.

From the study it is clear that even though these industries are capable to meet the range limit given by Central Pollution Control Board they are not efficient in the management of wastewater generated by them. It may be due to increase in the waste production day by day which makes the existing technologies inefficient. The discharge of effluents from the seafood industries badly effects the environment. Variation in the conductivity and salinity from their usual range is an indication of pollution. Most of the aquatic species have adapted to specific salinity levels. And also depletion of DO and increased concentration of BOD & COD cause stress on aquatic organisms, making the environment unsuitable for life. The authorities should be concerned about this and should pay attention in order to decrease the pollution created by the discharge of seafood industrial effluents.

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