ANALYSIS OF PHYSICOCHEMICAL PARAMETERS OF INDUSTRIAL EFFLUENT FROM HEBBAL AREA

Jamuna M

Postgraduate Department of Chemistry, Maharani's Science College for Women, JLB Road, Mysore-570 005, Karnataka.
Email ID: virgan2126@gmail.com

Abstract:
Water is the most important in shaping the land and regulating the climate. It is one of the most important compounds that profoundly influence life. The quality of water usually described according to its physical, chemical and biological characteristics. Due to rapid industrialisation, daily industries are discharging polluted water causing heavy and varied pollution in aquatic environment leading to depletion of aquatic biota. Due to this contaminated water human suffers from water borne diseases. It is therefore necessary to check the water quality by physic-chemical parameters like pH, conductivity, alkalinity, acidity, DO, BOD, COD, sulphate, chloride, nitrite-nitrates etc. The present work has been carried out to know the physico-chemical contents in the industrial effluent from Hebbal area. The concentration of calcium and magnesium is 94.18 ppm and 94.12 ppm respectively. The values are greater than WHO rating i.e., 2.5 ppm. Hence it causes hardness of water. Sulfate is lower 33.62 ppm compared to WHO rating 62.5 ppm. It doesn't cause dehydration. The concentration of nitrite was found to be 0.09 ppm lower than WHO rating 12.5 ppm, indicating not harmful to the environment. Concentration of chloride content in the given water sample was found to be 162.94mg/100ml. In the industrial effluent, the concentration of chloride is 162.94 ppm greater than WHO ranging 62.95 ppm. High level of chloride can have negative impact on an ecosystem. Hence the above industrial effluent cannot be released into any water bodies without treatment.

INTRODUCTION

Water is made up of two hydrogen atoms and one oxygen atom. It has the formula H_2O. When oxygen and hydrogen combine (H-O-H) they form V-shaped triangular molecule. Water molecules attracted to each other, creating hydrogen bonds. These strong bond determine almost every physical property of water and many of it's chemical properties too. Water is the solvent, the medium and the participant in most of the chemical reaction occurs in the chemical reaction in our environment [1]. Water molecule have a tendency to ionize they dissociate into ions (charged particles) hydrogen ions (H^+) and hydroxide ions (OH^-). A neutral solution contains an equal number of hydroxide ions and hydrogen ions. A solution with a greater concentration of hydrogen ions (H^+) is said to be acidic. A solution with greater concentration of hydroxide ions (OH^-) is said to be alkaline or basic [2].

Water covers 71% of the Earth's surface, and is vital for all known forms of life. On Earth, 96.5% of the

planet's water is found in oceans,1.7% in groundwater, 1.7% in glaciers and the ice caps of Antartica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapour, clouds(formed of solid and liquid water particles suspended in air), and precipitation [3]. Only 2.5% of the Earth's water is fresh water, and 98.8% of that water is in ice and groundwater. Less than 0.3% of all freshwater is in lakes rivers, and atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products [4].

Evaluation of water pollution status and pollution levels can be indicated by several indicators, which can be divided into two specific categories: One is physical and Chemical indicator, the other is a composite indicator of organic pollution and nutrients [5].

PHYSICAL AND CHEMICAL INDICATOR

Physical and chemical properties of water temperature are closely related. Water temperature changes with biological and microbial activity, non-ionic ammonia, salinity and pH. Pure water is colourless and transparent. Clean water, should be colorless. Waste water generated from textile, printing and dyeing, paper making, food, organic synthesis industries often contains a lot of dye, biological pigments and coloured suspended particles, constituting the major way of water pollution by coloring the water body [6]. These polluted water lead into water body it affects the growth of aquatic organisms. Water is a liquid. Odour in water is usually measured in terms of it's Threshold odour number (TON) [7]. Some organic and inorganic materials generated by foul water come mainly from domestic and industrial sewage, decomposition of natural materials, or the activities of micro-organisms and biological organisms. Turbidity is to describe water containing silt, clay, organic, inorganic, and suspended materials such as plankton and micro-organisms, the sediment of which is not only slow but difficult [8]. As the turbidity caused by iron and manganese hydroxide is

very harmful to human life, we must use special methods to remove them. Natural water, after going through the process of coagulation, sedimentation and filtration treatments, can become clear water. pH refers to the negative logarithm of hydrogen ion activity in water. $pH=log[H^+]$. The pH value of natural water is usually between 6 and 9, which is also a controlled scope of the pH value for our wastewater discharge. Not only is pH closely related to water solubility, chemical form, attribute, activities and effects, but it also has a significant impact on the activities of aquatic life [9].

The total residue refers to the material left in the containers after evaporation or drying of water or sewage in a certain temperature, including the " unfilterable residue"(all the residue that is trapped in the filter, also known as suspended solids) and "filterable residue"(all residues that can go through the filter, also known as soluble solids). Suspended solids can affect the transparency of water, reduce photosynthesis of algae in water [10], restrict the normal movement of aquatic organisms, slow underwater activity, result in hypoxic the bottom of the water, and reduce the assimilation ability of water body. Acidity refers to all substances in the water neutralising alkali, i.e. total amount of materials which release H^+ or generate H^+ through the hydrolysis. In the surface water, the integration of CO_2 or discharge of acid-containing wastewater by machinery, mineral processing, electroplating, pesticides, printing and dyeing, chemical and other industries shall result in lower pH in the water body. Therefore, the acidity is an important indicator in the measurement of the change after bodies [11]. The sum of components mainly bicarbonates, carbonates and hydroxides in the water contributes to the alkalinity in water that tends to elevate the pH of the water above 6.5. Alkalinity above 75 mg/L to offset acid produced by bacteria nitrifying ammonia [12,13]. The acceptable range for most fishing is 20-200 mg/1 ppm. The level of oxygen gas dissolved in water (DO) is vital for the survival of most aquatic organism as it's provides them with oxygen to carryout cellular respiration [14, 15]. It is therefore

an important indicator of the quality of water. Chemical oxygen demand (COD) refers to the amount of oxidant consumed in the oxidation of water sample in the specified condition [16, 17]. Chemical oxygen demand reflects the contamination degree of the restored materials in water which include organic matter, nitrite, ferrous salt, sulphide and so on [18, 19]. It is common for water to be contaminated; therefore, COD can also be used as an indicator of relative content of organic matters, was organic pollution is very common. Therefore, the chemical oxygen demands also a condition indicator. China uses potassium dichromate method in testing wastewater, the measured value of which is called chemical oxygen demand [20, 21]. BOD is the amount of dissolved oxygen needed by aerobic biological organism in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. Domestic sewage and industrial waste water contains large amount of organic matters in various forms [22, 23]. When the waters are polluted, the decomposition of organic matters in the water would consume a lot of dissolved oxygen, and there by undermining the balance of oxygen in water, deteriorating water quality and causing death to fish and other aquatic organisms because of hypoxia. Organic matters in water, and biochemical oxygen demand is one of the important indicators fall into this category [24, 25].

It is very essential to analyse the industrial effluent for various physico-chemical parameters such as pH, conductivity, alkalinity, acidity, DO, BOD, COD, sulphate, chloride, nitrite-nitrates etc. The present work has been carried out to know the physico-chemical contents in the industrial effluent from Hebbal area.

MATERIALS AND METHODS

Chemicals: All the chemicals used were of analytical grade. It includes Barium chloride, EDTA, $MgCl_2$, Erichrome black – T indicator, KOH, $K_2Cr_2O_7$, Sulphanyl amide solution, Naphthyl ethylene diamine dihydro chloride, PHP, Methyl orange indicator, Phenolphthalein indicator, silver nitrate etc.

The initial sample collected from the target population without any processing from an industry located in Hebbal indusrial area, Mysuru. Homogeneous solutions are easily sampled by siphoning, decanting, or by using a pipette or syringe. For heterogeneous solution, manual shaking is often sufficient to ensure homogeneity.

1. Analysis of sulfate by complexometric titration using EDTA (indirect method): Pipette out 10mL of the sulfate ion solution into small beaker, dilute to 50mL and adjust the pH to 1 with 2M HCl, heat nearly to boiling point. Add 15mL of the nearly boiling $BaCl_2$ solution, fairly rapidly & with vigorous stirring heat on a steam bath for 1 hour, filter with whatmann filter paper no 42. Wash the precipitate with cold water, transfer the filter paper precipitate quantitatively to the original beaker. Add 32mL of standardized 0.05M EDTA solution. 5mL of concentrated ammonia solution and boil gently, after 10-15 minutes to facilitate the dissolution of the precipitate cool the resolving clear solution, add 10mL of the buffer solution (pH -10), a few drops of Erichrome black –T indicator and titrate the excess of EDTA with standard magnesium chloride solution to a clear red colour.

2. Analysis of calcium and magnesium by complexometric titration using EDTA
Standardization of EDTA solution: 10mL of $ZnSO_4$ solution was pipette out into a clean Erlenmeyer's flask. About 3mL of buffer (NH_3-NH_4Cl pH-10) was added followed by few drops of Erichrome black-T indicator and titrated EDTA solution till the colour change from wine red to blue colour. The readings were recorded.

Procedure for the determination of Calcium and Magnesium in a mixture: To10mL of water sample, 3mL of buffer was added followed by the few drops of Erichrome black –T indicator and the contents in the Erlenmeyer's flask were titrated against standardized EDTA solution till the colour

changes from wine red to blue indicating the end point and the titration was repeated for concordant values and the concentration of Ca and Mg was calculated.

Determination of Calcium alone: 10mL of the water sample was pipette out in to a clean Erlenmeyer's flask, 3mL of 8M KOH was added followed by the addition of few drops of Patton Reeder's indicator and the contents of the flask was titrated against standardized EDTA solution till the colour changes from wine red to blue and the titre value recorded and the titration was carried out for concordant values of calcium alone.

3. Analysis of dissolved oxygen and Chemical oxygen demand by titrymetry:

a. Dissolved Oxygen: Pipette out 20ml of water sample into a clean conical flask, about 1mL of $MnSO_4$ solution and 2mL of alkaline KI solution was added and shaken well. Then 1mL of 10% KI and 2mL of conc. H_2SO_4 was added. This mixture was titrated against standard thiosulphate solution using starch as an indicator. The amount of dissolved oxygen was calculated using a relation 1mL of $Na_2S_2O_3 = 8mg$ of dissolved oxygen.

b. Chemical oxygen demand: About 20mL of water sample was pipette in to a clean conical flask, about 10mL of 0.25N $K_2Cr_2O_7$, a pinch of Ag_2SO_4 and $HgSO_4$ and 20mL of H_2SO_4 was added to the flask and refluxed for 2-3 hours. Then it was cooled, diluted and titrated against standard ferrous ammonium sulfate using indicator until the colour changes blue to red.

4. Analysis of nitrite – nitrogen by spectrophotometry: To a series of 25mL volumetric flask 0.25, 0.5, 0.75, 1.25, 1.5mL of 10ppm nitrite solution was pipette out, to it 2mL of sulphanylamide was added and allowed to stand for 10minutes. To this 2mL of naphthyl ethylene diamine dihydro chloride was added and allowed to stand for 10 min and the absorbance was recorded and a graph of absorbance v/s concentration of nitrite was plotted from which the concentration of nitrite in the sample was determined.

5. Analysis of total acidity by pH and conductometric titration and comparison with visual methods:

a. Visual method: Determination of methyl orange acidity: Accurately 10mL of waste water was pipette into a conical flask and drops NaS_2O_3 was added. This mixture was titrated against 0.1N NaOH using 2drops of methyl orange indicator until red colour changes from red to yellow. Titration was repeated for concordant values and concentration of acid content was calculated.

Determination of Total acidity (or) phenolphthalein acidity: 10.0mL of waste water sample was pipette into 100mL Erlenmeyer's flask and few drops of 1% $Na_2S_2O_3$ followed by few drops of phenolphthalein indicator was added and against standardized NaOH solution taken in a burette till pink. Titration was repeated to get the concordant volume and from the titre value and concentration of acid content for was calculated.

b. By pH metric method: Pipette out 20mL of sample into another 100mL volumetric flask diluted upto the mark using distilled water. The dual electrode was connected to pH –meter calibrated by using buffer- 4 and 7 tablet solution. After calibration 25mL of water sample was pipette out into 100mL beaker containing glass rod and a dual electrode. This solution was titrated with NaOH solution taken in the burette. The pH readings were noted after each addition of NaOH (0.5mL). The titration was continued up to the 2nd end point. In this experiment we have got 2jumps which gives the equivalence point. A graph of pH v/s volume of NaOH added was plotted and the concentration of waste water sample was calculated.

c. By conductivity method: 10.0mL of industrial effluent sample was pipette into a beaker provided with glass rod and a conductivity cell connected to conductometer. Initial conductance was recorded. The NaOH was added from the burette in 0.5mL

intervals and conductance was noted after each addition. The graph of conductance V/s volume of NaOH added was plotted. From the graph total acidity was calculated.

6. Analysis of industrial effluent for alkalinity by pH and conductometric and comparison with visual method:

a. Determination of Methyl-Orange alkalinity: 10.0ml of waste water sample was pipette out into 100ml Erlenmeyer's flask and a drop of $Na_2S_2O_3$ solution was added followed by a drop of methyl orange indicator and this was titrated against standardized HCl solution taken in the burette till the colour changes from yellow to red. titration was repeated to get concordant volumes and from the value. The total alkalinity was calculated.

b. By p^H method: 20.0ml of waste water sample was pipette out into another 100ml volumetric flask and it was diluted to 100ml using distilled water. The dual electrode wash with distilled water and it was connected to pH meter. The pH meter was calibrated by using buffer-7 and 9.2.

After calibration, 25 ml of waste water sample was pipette out into a 100ml beaker containing glass rod and a dual electrode which was connected to pH meter. The solution in beaker was titrated with standardized HCl solution in the burette. The pH-reading were noted after each addition of HCl. The titration was continued up to 2nd end point. A graph of pH V/s volume of HCl added was plotted and the total alkalinity was calculated.

c. By conductometric method: 10.0 ml of industrial effluent sample was pipette into a beaker and provided with a glass rod and a conductivity cell connected to conductometer. The initial conductance was recorded. HCl was added from burette in 0.5 ml interval conductance was noted after each addition of HCl and was continued till the 2nd equivalence point. A graph of conductance v/s volume of HCl added was plotted from the graph, total alkalinity was calculated.

7. a. Analysis of chloride content by spectrophotometry (mercuric thiocyanate method): Into a series of calibrated flask 2.5, 5.0, 7.5, 10.0, 12.5 ml of chloride solution (working standard 10ppm) was added, and 2ml of 0.25 ml of Fe(II) solution which must be dissolved in 9M nitric acid followed by 0.5 ml of mercury (II) thiocyanate (saturated solution of mercuric thiocyanate in ethanol) were added and diluted up to the mark chloride free water. The absorbance of all the solutions was measured at 460 nm [26]. A graph of absorbance v/s Concentration of Chloride ion was plotted. From the calibration graph, concentration of chloride in the given test sample was determined.

b. Analysis of industrial effluent for chloride content by conductometric titration: 10.0 ml of chloride solution was pipette in a beaker the conductivity cell was placed in it. The conductance was measure after each addition of AgNO3 (0.5 ml at each intervals) taken in the burette. The titration was continued till the change in the conductance was observed. A graph of a Conductance v/s volume of $AgNO_3$ added was plotted and the end point was located from which, chloride content in the given water sample was calculated. Given: 1 mL of 1 M $AgNO_3$=35.5mg of Cl

c. Analysis of industrial effluent for chloride content by potentiometric method: Ten mL of the water sample was pipette into a small beaker and silver electrode was placed in it. A cell was conducted with silver electrode and calomel electrode using KNO_3. Salt bridge silver nitrate solution was taken in the burette was added in steps of 0.5 ml into the water sample. After each addition, the solution was stirred well and the emf was noted. A graph of $\Delta E/\Delta V$ V/S $AgNO_3$ added was plotted from the graph, the concentration and amount of chloride present in the given industrial sample was calculated.

8. Spectrophotometric determination of flouride in industrial effluent: Take 0, 1, 2, 3, 4 and 5 ml of 100 ppm flouride solution in a series of 25 mL volumetric flask (in a 10 mL burette) add drop wise

of arsenite solution to each flask and 1 mL of zirconyl acid solution and alizarin red solution. Dilute to 25 mL distilled water. Measure the absorbance of each solution after 15min at 530 nm v/s water as blank. Treat a suitable aliquot (2.5 or 10ml) depending on the fluoride concentration in the same manner and measure the absorbance at 530nm. Prepare the calibration curve by plotting absorbance v/s ppm in 530 nm. Read the concentration of fluoride from the graph and report the fluoride concentration in the industrial effluent tested.

RESULTS AND DISCUSSION

Titration also known as titrimetry is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte. This method includes the use of indicators, and it is simple, low cost and safe method which can be used in determining metals concentration in any environment samples under ordinary laboratory level. In the present study the amount of sulfate ion in the given industrial effluent was found to be 33.62ppm. In the Industrial effluent, the concentration of sulfate is lower 33.62 ppm compared to WHO rating 62.5 ppm. Hence, it is lower than permissible limit. It doesn't cause dehydration.

In the industrial effluent, the concentration of calcium and magnesium is 94.18 ppm and 94.12 ppm respectively. The values are greater than WHO rating i.e., 2.5 ppm. Hence it causes hardness of water.

The dissolved oxygen in the sample was found to be 0.8ppm. The chemical oxygen demand in the sample was found to be 131.55ppm. According to WHO dissolved oxygen in a stream water may vary from 0 mg/L to 18 mg/L. But reduced DO level leads to warming up of water and also indicative of too many bacteria.
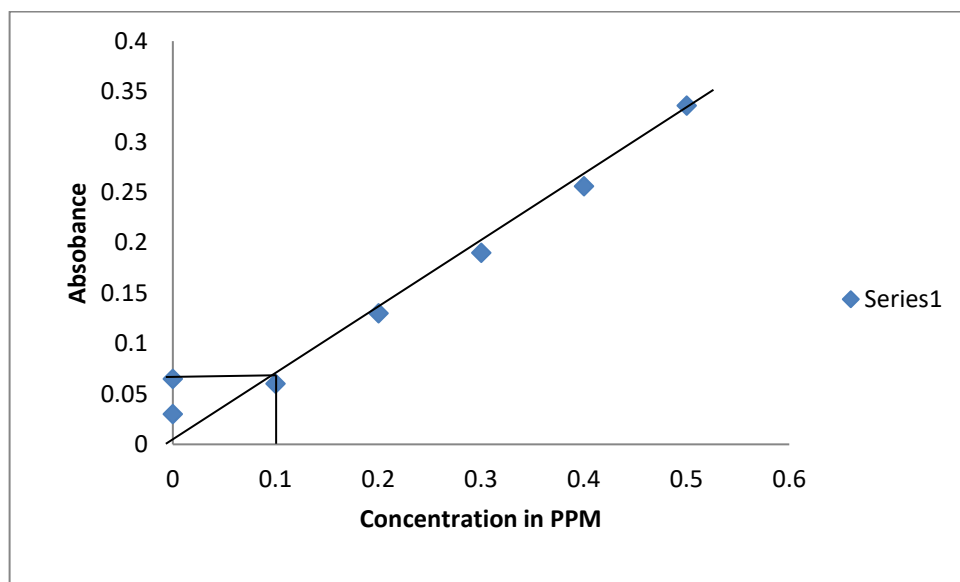

Figure: 1. Determination of nitrite by spectrophotometry.

Spectrophotometry is the quantitative measurement of the absorption or transmission properties of material as a function of wavelength. Colored solution can be analysed. These methods are used in industries including semiconductors, laser and optical manufacturing etc. It is used in ordinary laboratory for the study of chemical substance present in different water samples. It is a method which is economically viable and posess less i.e. economically viable and processes less hazarders. In the industrial effluent, the concentration of nitrite determined by spectrophotometry method was found

to be 0.09 ppm lower than WHO rating 12.5 ppm (figure 1). Hence, nitrite content is lower than permissible limit indicating not harmful to the environment.

Methyl orange acidity was found to be 2700 ppm, while phenolphthalein acidity was found to be 11.7 ppm.
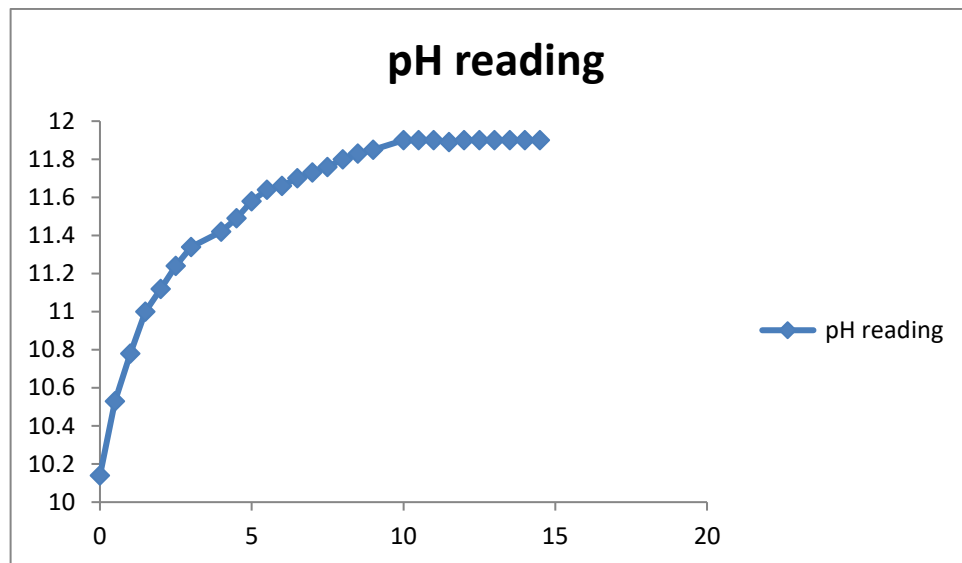
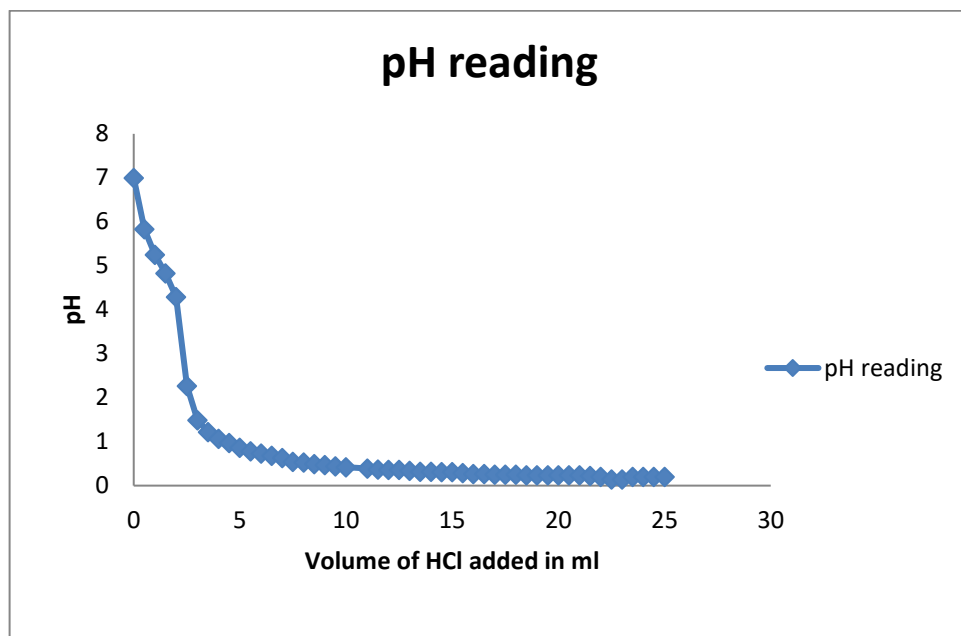**Figure: 2. Determination of total acidity by pH Method**

From the figure 2, it was found that the sample is not acidic in nature, since the pH value remains constant even after the addition of excess of alkali.
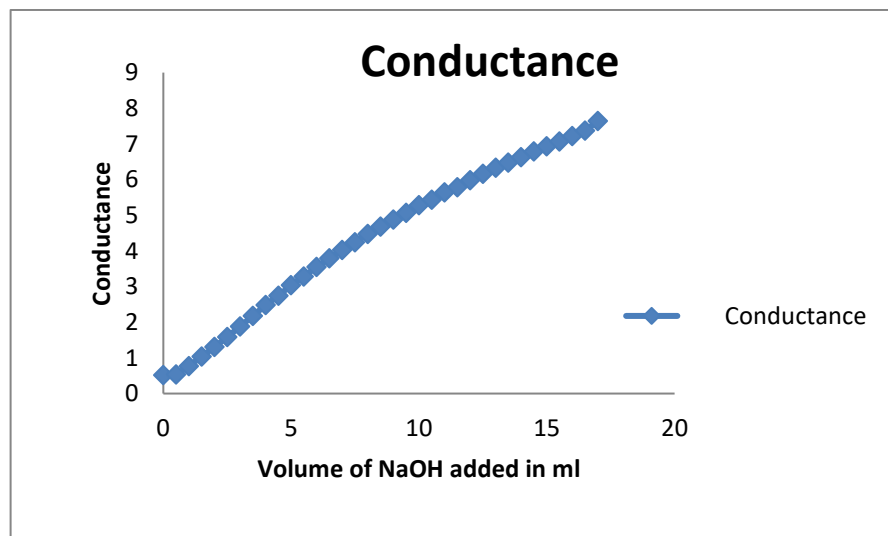
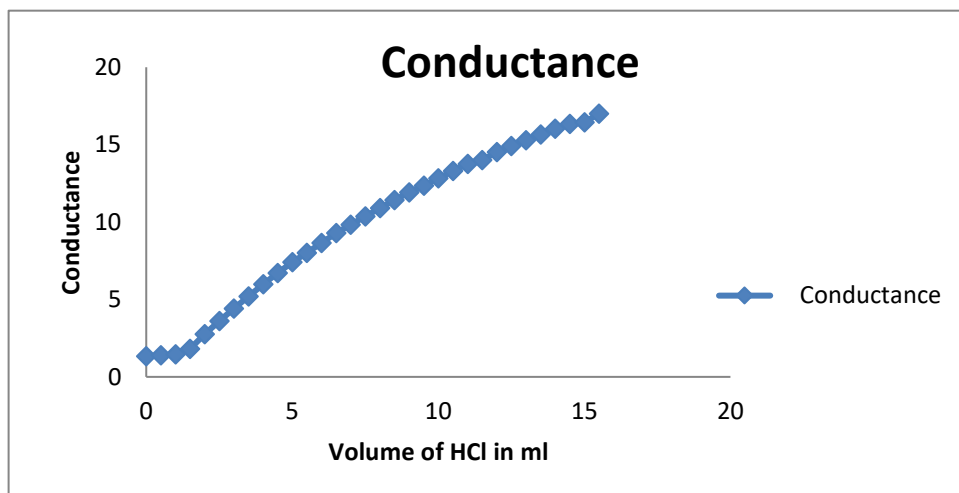**Figure: 3. Determination of Total Acidity by Conductivity Method**

The given sample is not acidic. From the figure 3, it was observed that conductivity goes on increasing on adding NaOH solution. This indicates that the sample's conductivity increasing due to increasing in highly mobile Na^+ ions. The phenolphthalein alkalinity reveals 1683.5 ppm. The methyl orange alkalinity exhibits 455 ppm.

Figure: 4. Determination of alkalinity by pH metric method.

From the graph (figure 4), the pH of the given sample goes on decreasing and pH reading starts from 7 so the alkalinity seems to be negligible.


Figure 5. Determination of total alkalinity by Conductivity method

Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added the equivalence point is the point at which the conductivity undergoes a sudden change i,e. marked increase or decrease in conductants. From the graph (figure 5), the conductivity goes on increasing, indicating alkalinity was not found in the given sample. The given sample doesn't contain any alkaline sources because pH reading starts from 7 and goes on decreasing so there is no alkalinity.
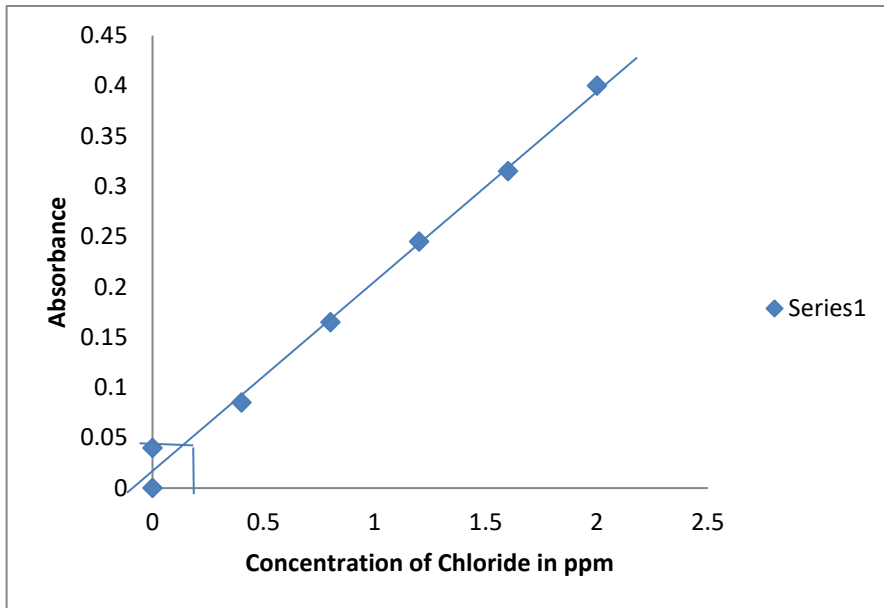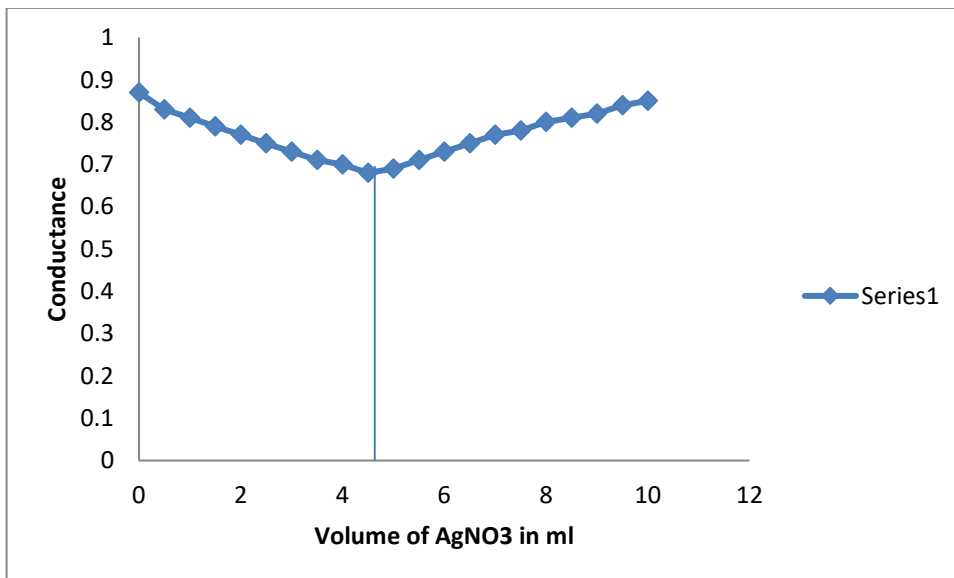
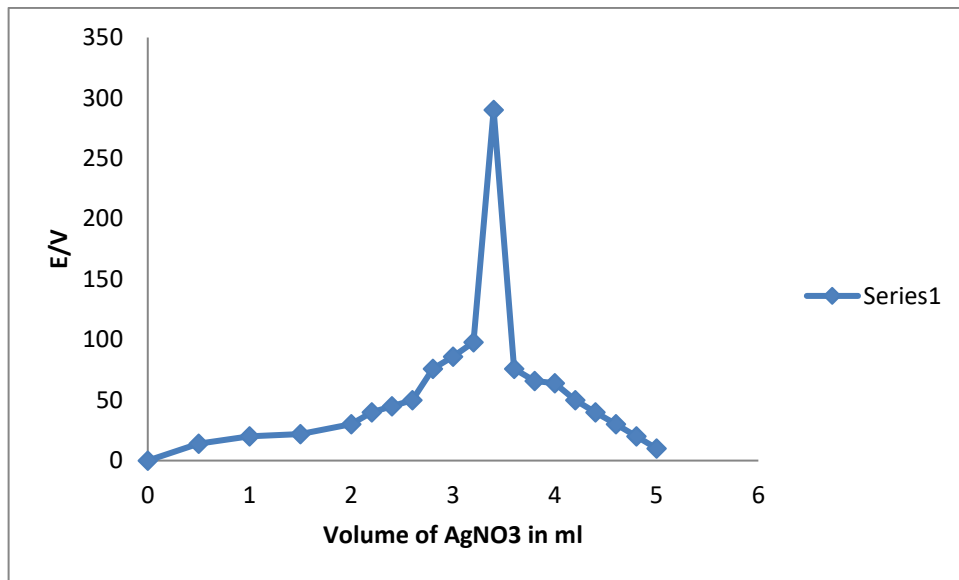**Figure 6. Determination of Chloride by Spetrophotometric method**

The concentration of chloride in the given sample is 3.4 ppm (from figure 6), lower than WHO rating 62.5 ppm.

From graph (figure 7), concentration of Chloride content in the given water sample was found to be 162.94mg/100ml. In the industrial effluent, the concentration of chloride is 162.94 ppm greater than WHO raring 62.95 ppm. Hence chloride content is greater than permissible limit.


Figure: 7. Determination of Chloride by Conductivity method

Figure: 8. Determination of Chloride by Potentiometric method

Potentiometric measurement involves the measurement of the potential of suitable indicator electrodes as a function of titrant volume. These measurements use a rapid change in potential near the equivalence point. Thus, we can measure the equivalence point accurately without using any indicator. Similarly in the case of pH metric method, we measure the change in pH as a function of titrant volume. These methods involve some electrodes which are expensive but in ordinary laboratory level can be perform with less hazarder. From graph, as depicted in figure 8, the concentration of chloride content in the given water sample 123.1ppm, is greater than WHO rating 62.95 ppm. High level of chloride can have negative impact on an ecosystem.
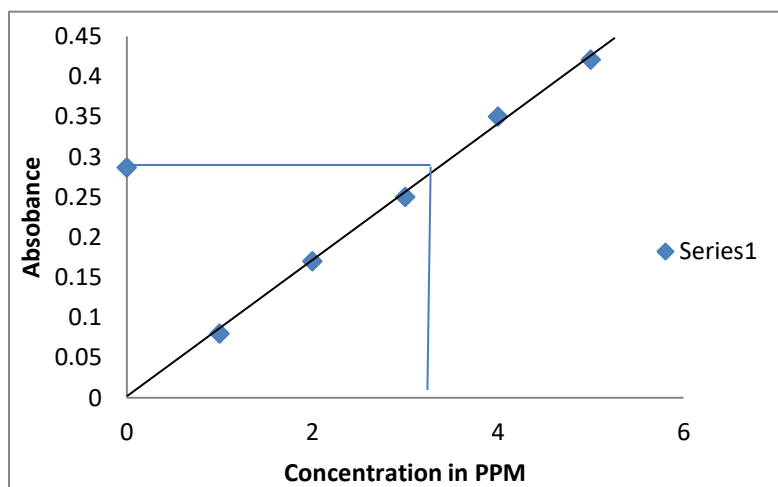
Figure: 9. Determination of Fluoride by spetrophotometric method

The concentration of fluoride was 0.3 ppm is lower than WHO rating 0.375 ppm.

Table: 1. Comparison of chemical constituents with WHO standards

Chemicals constituents	Method	Experimental value	WHO standards
Sulfate	Visual method, EDTA indirect titration	33.62 ppm	62.5ppm
Calcium	Visual method, EDTA direct titration	94.18 ppm	2.5ppm
Magnesium	Visual method , EDTA direct titration	94.12 ppm	2.5ppm
Nitrite	Spectrophotometry	0.09 ppm	12.5ppm
pH		7.0	6.5-8.5
Chloride	1.Spectrophotometry 2.Conductometric titration 3.Potentiometric titration	3.4 ppm 162.94 ppm 123.1 ppm	62.5ppm
Fluoride	Spectrophotometry	0.3 ppm	0.375ppm

The present study was undertaken with aim to analyse certain physico-chemical parameters in the industrial effluent. In nutshell the parameters analysed have shown species which are present in higher rating the WHO reading (calcium, magnesium and chloride) these chemical constituents enters into the water and causes the pollution for surface water and ground water. These metals also destroy the ecosystem in which they enter. In the present investigation the potability of industrial effluent with respect to fluoride, nitrite, sulfate, etc was compared with the standards set by WHO for different chemicals involved as shown in the table 1.

Acknowledgment

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