CHAPTER - IV

PHYSICO-CHEMICAL CHARACTERISTICS OF LEATHER TANNERY EFFLUENTS

Human civilization originated, developed and thrived in places within easy reach of fresh water sources. Amongst global resources, water is emerging as perhaps the most critical but misused natural resource\(^1\). Water is the elixir of life without which no biota could survive in the biosphere. The industrial growth in Dindigul town though solving economic problem, also add up to environmental pollution as waste water effluents from tanneries are discharged into water bodies deteriorating the water quality\(^2\). The discharge of industrial effluents, besides increasing the dissolved residues, which increase the total amount of sediments, also bring about chemical transformation in soils continuously irrigated by polluted waters\(^3\). As a result of this, serious biological and ecological instability may occur as more and more industrial wastes are thrown out into the bodies of water.

Industrial pollution is a global concern. Among the major different industries, the tanning industry is a notorious polluter of the environment. The tannery effluent pollutes soil and ground water if washed into the river. Tannery effluent is the untreated waste water of tanneries. It appears as dull grey colour with the odour of the hydrogen Sulphide. It contains the preliminary hairs of animals. Pollutants are blood, fat, pieces of flesh, soil particles of other biological origin. In the tanning process, various inorganic and organic chemicals like Chloride, Sulphides, Tanoloin (16 % chromium) and titanium dioxides are used\(^4\). The tannery effluents contain high concentration of metallic ion like Chromium, Potassium, Sodium and Magnesium and organic pollutants like oil and grease, tannin and lignin\(^5\). Tannery is one of the major water consuming industrial responsible for water pollution problem of considerable magnitude, since most of the water discharged as waste water.

The most often affected natural resource is our water resources, which is used to dispose our industrial and domestic wastes\(^6\). Effluents discharged from leather tannery contains a number of chemical pollutants such as Carbonate, Bicarbonate, Nitrite, Phosphate, oils and grease in addition to Total suspended solids, volatile solids and score of other toxicants. These pollutants could bring about changes in temperature, humidity, oxygen supply, pesticide stress amounting to a partial or complete alteration in the physical, chemical and physiological spheres of the biota\(^7\). When the untreated effluents are discharged into the environment, they disrupt the ecosystem\(^8\).
Water quality is the term widely used in multiple scientific publications and normative documents relating to the necessities of “sustainable” and “optimal” management of water resources. The water quality index (WQI) has been considered to give criteria for surface water classification based on the use of standard parameters for water characterization. This index is a mathematical instrument used to transform large quantities of water characterization data into a single number, which represents the water quality level.

The primary objectives of the present study are to assess the effluent from the leather tanneries to characterize and to find out the correlation co-efficient for all the possible correlation among water quality parameters. Analysis of any monitored parameter either in alone or group according to a common feature, provides partial information on the overall water quality. In this study a data matrix obtained during the monitoring period October 2010 to March 2011 is subjected to water quality index to assess and to classify water quality from multiple measured parameters.

4.1 EXPERIMENTAL METHODOLOGY

The study area is located in the southern part of India, close to Kodaganar river basis, mainly in hard rock terrain. The area is known for its leather industries. It lies between 10°13'44" – 10°26'47" N latitude and 77°55’08” – 78°01’24” E longitude and falls in survey of India Top sheet No.58 F/15 & J/3, in the state of Tamil nadu, India. The selected area is located in the central part of Dindigul town and along Madurai, Batlagundu and Ponmadurai by pass roads. Selections of sampling locations are listed in table 4.1.

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Site</th>
<th>Location Description</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Thomaiyarpuram bypass</td>
<td>Tanneries, Small scale industries</td>
<td>Industrial (Tannery area)</td>
</tr>
<tr>
<td>2.</td>
<td>Dindigul Bus stand</td>
<td>Traffic, hotels, shopping complex, theatre, commercial complex, market</td>
<td>Commercial cum Traffic</td>
</tr>
<tr>
<td>3.</td>
<td>Lakshmanapuram</td>
<td>Residential areas of lower and middle classes, small shops</td>
<td>Residential</td>
</tr>
</tbody>
</table>

4.1a COLLECTION AND ANALYSIS OF WASTE WATER EFFLUENT

Tannery effluent samples were collected from the discharged stream of tannery effluent situated in Dindigul town of India twice in a month from October 2010 to March
2011. During sampling, the samples were collected in a 2 liter polythene carbuoys and mixed in equal proportions to get uniform homogeneous samples\textsuperscript{10}. Random selection procedure was adopted for the selection of both sampling unit and the sampling point in a given site\textsuperscript{11}. Tap water and 8M HNO\textsubscript{3} were used to wash the polythene bottles of 100ml capacity, which is used for the sample preservation followed by washing it with distilled water and finally with double distilled water\textsuperscript{12}. Then, the bottles were rinsed thrice with effluent samples and the effluent samples were stored in a refrigerator at 4°C, after adding the necessary preservatives. Preservatives are essential for retarding, biological action, hydrolysis for chemical compounds and complexes and reduction of volatility of constituents for measuring COD, H\textsubscript{2}SO\textsubscript{4} was added to bring pH to two and then preserved. For phosphates, 20mg mercuric chloride was added and refrigerated. During analysis the mixed, homogeneous effluents after reservation were taken out from the refrigerator. These samples were used for analysis of water quality parameters according to the standard methods reported in literature\textsuperscript{12}.

The other parameters such as temperature, pH and electrical conductivity were determined in the field itself (within 30 minutes). The other water quality parameters were determined within 82 hours except BOD, which was determined only after 5 days of incubation at 20°C.

The data set taken in this study is comprised of twenty four parameters such as water Temperature, pH, Turbidity, TDS, Electrical conductivity, Alkalinity Total as CaCO\textsubscript{3}, Total hardness as CaCO\textsubscript{3} Calcium, Magnesium, Sodium, Potassium, Iron total, free Ammonia, Nitrite, Nitrate, Dissolved oxygen (DO), Total Chromium, Biological oxygen demand, Chemical oxygen demand, Total Suspended Solids, Chloride, Fluoride, Sulphate and Phosphate. These parameters were chosen as they have verified weight factors for different ranges of the parameters to calculate water quality index in various literatures\textsuperscript{13}.

4.2 MATERIALS AND METHODS

1. COLOUR

Colour of the sample can be compared with known colour standards.

2. ODOR

Odour is generally measured as “threshold odour number” which is equal to dilution ratio of the sample at which the odour is just detectable. The sample is diluted with odour free water until a least perceptible odour is detected by the tester. As the sensitivity to odour of different persons varies, therefore, minimum five persons and preferably ten or more should observe the samples for odour. These persons should not suffer from cold or any such disease which interferes with the sense of smell.
3. TEMPERATURE

For determination of sample water temperature, collect water in some suitable container. Soon after collection of the sample, insert a mercury thermometer and note the reading. The thermometer should be of small thermal capacity to attain equilibrium rapidly and must be graduated up to an accuracy of 0.1 to 0.2°C. The accuracy of the thermometer may vary depending upon the type of analysis.

To minimize the errors, it is always essential to calibrate the thermometer with a thermometer of known accuracy. While taking the reading, the scale of the thermometer should be immersed in the water up to the level of mercury in the capillary column.

4. pH

Principle

pH is the negative log$_{10}$ of the hydrogen ion concentration in a solution. It can be measured by colorimetric methods using various indicators or paper strips. However, the use of colorimetric methods is less convenient and less accurate. For accurate measurement of pH, electrometric methods are used employing hydrogen ion sensitive electrodes.

Apparatus

There are a number of Makes and Models available for pH meters. Portable pH meters are operated by battery can also be obtained. The accuracy of pH can vary from 0.01 to 0.1 depending on the Make. Some pH meters employ, while others may have a combined glass and reference electrodes. Most pH meters also have a temperature compensation system to avoid the differences arising due to the different temperatures.

Procedure

1. Follow the instructions given by the manufacturer to use the pH meter.
2. Essential aspect to use all the pH meters is to calibrate it with suitable buffers. Ready buffers of pH values are also available in the market. Set the pH meter with a buffer whose value is near to the expected pH of the sample.
3. Buffers of different pH values can also be made in the laboratory in the following manner:
   a) Potassium hydrogen phthalate buffer: Dissolve 10.2 g of potassium hydrogen phthalate in water to prepare 1000 ml of buffer.
   b) Phosphate buffer: Dissolve 3.40 g of KH$_2$PO$_4$ and 4.45 g of Na$_2$HPO$_4$.2H$_2$O in water to prepare 1000 ml of buffer.
   c) Borax buffer: Dissolve 3.81 g of Na$_2$B$_4$O$_7$.10H$_2$O in water to prepare 1000 ml of buffer.
5. TURBIDITY

Principle

When light is passed through a sample having suspended turbidity, some of the light scattered by the particles. The scattering of the light is generally proportional to the turbidity.

The turbidity of a sample is thus measured from the amount of light scattered by the sample taking reference with standard turbidity suspension.

The determination of turbidity is interfered by the presence of debris and other settle able matter the true colour in the sample reduces the values of turbidity.

Apparatus and Reagents

A. Nephelometer (Turbidity meter): It measures the scattered light at the right angle of the path of incident light.

B. Sample tubes: These should be clean and made up of a colour glass. The tubes should be free of any scratch or etching.

C. Stock turbidity a) Dissolve 1.0 g of hydrazine sulphate (NH\(_2\)\(_2\)\(\cdot\)H\(_2\)SO\(_4\)) in distilled water to prepare 100 ml of solution. b) Dissolve 10.0 g hexamethylene tetramine (CH\(_2\))\(_6\)N\(_4\) in distilled water to prepare 100 ml of solution. Mix 5 ml of each of the above solutions in a 100 ml volumetric flask and allow standing for 24 hours at 25 ± 30°C. Dilute it to 100 ml mark. This is 400 NTU (Nephelometric Turbidity Units) suspensions. This solution can be kept for about a month.

D. Standard turbidity suspension: Prepare 40 NTU solutions by diluting 10 ml of stock solution to 100 ml. This solution should be prepared every week.

Procedure

1. For handling the Nephelometer, follow the instructions supplied by the manufacturer.

2. Set the instructions at 100 with 40 NTU standard suspensions. In this case every division on the scale will be equal to 0.4 NTU turbidity.

3. Shake thoroughly the sample and keep it for sometime to eliminate the air bubbles.

4. Put the sample in the Nephelometer sample tube and find out the value on the scale.

5. If sample is suspected to have more turbidity (more than 40 NTU), dilute it so that turbidity values come below 40 NTU and take the reading.

Calculation

Turbidity, NTU = Nephelometer reading \(\times\) 0.4 \(\times\) Dilution factor
6. CONDUCTIVITY

Principle

It is generally measured with the help of a conductivity meter having a conductance cell containing electrodes of platinum coated with Platinum black or carbon. These electrodes are mounted rigidly and placed parallel at affixed distance. Conductance, when measured between the electrodes having a surface area of 1cm\(^2\) and placed at a distance of 1 cm is called electrical conductivity and is the property of the water sample, rather than the measuring system. The term specific conductance is also used in place of electrical conductivity, but is an obsolete term.

Procedure

It is measured with the help of a conductivity meter. Follow the instructions supplied by the manufacturer.

1. 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.

2. Note the temperature of the sample and find out the factor 7 to convert the values at 25°C.

Calculation

\[
\text{Conductivity} = \text{Observed conductance} \times \text{Cell constant} \times \text{temperature factor at 25 °C}.
\]

7. TOTAL DISSOLVED SOLIDS (TDS)

Principle

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

Procedure

1. Take an evaporating dish and ignite it at 550±50 °C in a muffle furnace for about an hour, cool in a desiccators and weigh.

2. Filter the sample through glass fibre filter paper applying the suction.

3. Evaporate 100 ml of this filtered sample (or more in case the solids are less than 250 Mg/L) in the preweighed evaporating dish on a water bath or a hot plate having temperature not more than 98 °C.

4. Heat the residue at 103-105 °C in an oven for one hour and take the final weight after cooling in desiccators.
Calculation

\[ \text{TDS, mg/L} = \frac{(A-B \times 1000 \times 1000)}{V} \]

Where, 
- \(A\) = Final weight of the dish in g.
- \(B\) = Initial weight of the dish in g.
- \(V\) = Volume of sample taken in ml.

8. TOTAL SUSPENDED SOLIDS

Determine total suspended solids as the difference between the total solids and total dissolved solids.

\[ \text{TSS} = \text{TS} - \text{TDS} \]

9. ALKALINITY

Total alkalinity is the measure of the capacity of the water to neutralize a strong acid. The alkalinity in the waters is generally imparted by the salts of carbonates, bicarbonates, phosphates, nitrates, borates and silicates together with the hydroxyl ions in free state. However, most of the waters are rich in carbonates with little concentration of other alkalinity imparting ions.

Total alkalinity can be estimated by titrating the sample with a strong acid (HCl or H\(_2\)SO\(_4\)), first to pH 8.3 using phenolphthalein as an indicator and then further to pH between 4.2 and 5.4 with methyl orange or mixed indicator. In first case, the value is called as phenolphthalein alkalinity (PA) and in second case; it is total alkalinity (TA).

Reagents

A. Hydrochloric acid, 0.1 N: Dilute 12N concentrated HCl (sp. Gr. 1.18) to 12 times (8.34 → 100 ml) to prepare 1.0 N HCl. Dilute it further to make 0.1 N HCl (100 → 1000 ml). Standardize it against sodium carbonate solution.

B. Methyl orange indicator, 0.05%: Dissolve 0.5 g of methyl orange in 100 ml of distilled water.

C. Phenolphthalein indicator: Dissolve 0.5 g of phenolphthalein in 50 ml of 95% ethanol and add 50ml of distilled water. Add 0.05 N CO\(_2\) free NaOH solutions drop wise, until the solution turns faintly pink.

D. Sodium carbonate, 0.1 N: Dissolve 5.300 g of Na\(_2\)CO\(_3\) previously dried at 250 °C for about 4 hours, in distilled water to prepare 1 liter of solution.

Procedure

1. Take 100 ml of sample in a conical flask and add 2 drops of phenolphthalein indicator.
2. If the solution remains colorless, PA = 0, and total alkalinity is determined as described.
3. If the colour changes to pink after addition of phenolphthalein titrate it with 0.1 N HCl until the colour disappears at end point. This is phenolphthalein alkalinity (PA).

4. Now add 2-3 drops of methyl orange to the same sample and continue the titration further, until the yellow colour changes to pink at end point. This is total alkalinity (TA).

**Calculation**

PA as CaCO$_3$, mg/L = \((A \times \text{Normality}) \times \text{HCl} \times 1000 \times 50/\text{ml of sample}\)

TA as CaCO$_3$, mg/L = \((B \times \text{Normality}) \times \text{HCl} \times 1000 \times 50/\text{ml of sample}\)

Where,  

- \(A\) = ml of HCl used with only phenolphthalein
- \(B\) = ml of total used with phenolphthalein and methyl orange

PA = Phenolphthalein alkalinity

TA = Total alkalinity

Concentration of carbonates, bicarbonates and hydroxyl ions can be determined data of PA and TA.

**10. HARDNESS**

**Principle**

Hardness is generally caused by the calcium and magnesium ions present in water. Polyvalent ions of some other metals like strontium, iron, aluminum, zinc and manganese are also capable of precipitating the soap and thus contributing to the hardness. However, the concentration of these ions is very low in natural waters, therefore, hardness is generally measured as concentration of only calcium and magnesium (as calcium carbonate), which are far higher in quantities over other hardness producing ions.

Calcium and magnesium form a complex of wine red colour with Eriochrome Black T at pH of 10.0 ± 0.1. The EDTA has got a stronger affinity towards Ca$^{++}$ and Mg$^{++}$band, therefore, by addition of EDTA, the former comes is broken down and a new complex of blue colour is formed.

**Reagents**

A. EDTA solution, 0.01 M  
Dissolve 3.723 g of disodium salt of EDTA in distilled water to prepare 1 litre of solution.  
Store in polyethylene or Pyrex bottle.

B. Buffer solution

   a. Dissolve 16.9 g ammonium chloride (NH$_4$Cl) in 143 ml of concentrated ammonium hydroxide (NH$_4$OH).
b. Dissolve 1.179 g of disodium EDTA and 0.780 g of MgSO$_4$·7H$_2$O in 50 ml distilled water. Mix both (a) and (b) solutions and dilute to 250 ml with distilled water.

c. Eriochrome Black T (Solochrome Black T) indicator Mix 0.40 g of Eriochrome Black T, with 100 g NaCl (A.R) and grind.

C. Sodium sulphide solution

Dissolve 5.0 g of Na$_2$S·9H$_2$O or 3.7 g Na$_2$S·5H$_2$O in 100 ml of distilled water. Tightly close the bottle to prevent oxidation:

**Procedure**

1. Take 50 ml sample in a conical flask: If sample is having higher calcium, take a smaller volume and dilute to 50 ml Add 1 ml of buffer solution.

2. If the sample is having higher amounts of heavy metals add 1 ml of Na$_2$S Solution.

3. Add 100-200 mg of Eriochrome Black T indicator, the solution turns wine red.

4. Titrate the contents against EDTA solution: At the end point colour changes from wine red to blue.

**Calculation**

Hardness as mg/L CaCO$_3$ = ml EDTA used X 100/ ml of sample taken for titration

**Total hardness = Permanent hardness – Temporary hardness**

10. **DETERMINATION OF SODIUM AND POTASSIUM**

   Exactly 20 ml of each water sample was taken in a silica crucible and evaporated to dryness using steam bath and the heating continued in a muffle furnace at 550°C-600°C for 1 hour. The ash content were dissolved separately in a minimum quantity of concentrated HNO$_3$ and 10-15 ml of distilled water and filter through Whatman No.41 filter paper and made upto 100 ml, so that the final HNO$_3$ content was about 1%(W/V). The solution is used for estimation of Na$^+$ ion. Standard solution containing 0.1 to 40 ppm of Na$^+$ ion were prepared by diluting the standard solution of NaCl (100 ppm) and used for calculation of Flame photometer. The flame photometer (Systronics, Model No.130, India) scale reading for the blank (Pure distilled water) was set to be zero.

   Calibration curve was drawn by plotting flame photometer reading (MR) Vs Concentration of standard Na$^+$ ion. The water samples (HNO$_3$ acid digested and suitably diluted) were introduced into the burner unit of flame photometer and the meter readings (MR) were noted. From the calibration curve, the amounts of sodium ion present in the diluted water sample were determined by interpolation method. Finally the sodium ions present in the water sample were calculated.
A Series of standard containing 0.1 to 0.4 mg/l of potassium ion were prepared from the stock solution of KCl (100ppm). Flame photometer (Systronics, Model No. 130, India) was calibrated drawn by plotting flame photometer scale reading (MR) Vs Concentration of K⁺ ions. The water samples (HNO₃ acid digested and suitably diluted) were introduced into the burner unit of flame photometer. The flame photometer scale reading was noted, from the calibration curve the amount of K⁺ ions present in the water sample was determined by employing the interpolation method.

11. CALCIUM

Exactly 25 ml of water sample was taken separately in a clean, dry 250 ml conical flask and one ml of 20%(W/V) KOH solution was added to bring the pH of the water sample to 12. Then 0.5 g of pattern-readers indicator was added. The solution was titrated against standard EDTA (0.02N) until the end point colour change from wine red to blue colour. From the titre value calcium ion was calculated in ppm by using the following equation.

Total Calcium as CaCO₃ in ppm = \[\frac{A \times B \times 400.8}{V}\]

Where, A = Volume of EDTA consume by the water sample (ml), V = Volume of water sample taken (ml), B = mg of CaCO₃ equivalent to 1 ml of 0.02N EDTA titrant at the Calcium end point.

12. MAGNESIUM

Magnesium content present in water sample was determined by the complexometric method using EDTA as a complexing agent. Exactly, 25 ml of water sample was taken in a clean conical flask and 30 ml of calcium precipitating buffer solution (6 gm of ammonium oxalate in a 100 ml of water mixed with 144 gm of ammonium chloride and 13 ml of liquid ammonia solution and make up into 1000 ml) was added. The resultant solution was allowed to stand for half an hour and filtered through Whatman No. 45 filter paper. 1 ml of pH 10 ml buffer solution (NH₃ and NH₄Cl) was allowed to the filtrate solution followed by the addition of 2 drops of EBT as indicator. This solution was further titrated against standard 0.02N EDTA solution until solution the end point colour change from wine red to purple blue. From the titre value, the Mg²⁺ content was calculated in Mg/l or ppm.

Total Magnesium as CaCO₃ in ppm = \[\frac{A \times B \times 1 \times 1000}{V}\]

Where, A = Volume of EDTA consumed by the water sample (ml)  
V = Volume of water sample taken (ml)  
B = mg of CaCO₃ equivalent to 1 ml of 0.02N EDTA titrant at the Mg²⁺ end point.
13. SULPHATE

Exactly 25 ml of water sample was taken separately in a clean, dry 100 ml conical flask and one ml (1:1) HCl solution was added. After boiling for about 1 minute, 5 ml of 5% (W/V) BaCl₂ solution was slowly added with constant stirring. The precipitate was filtered through the previous weighed sintered glass crucibles (G-4), washed with hot water and the sintered glass crucible was dried in a air – oven at 105°C, cooled desiccators and weighed until the concordant values of weight was obtained. The following reaction is involved.

\[
\text{SO}_4^{2-} + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + \text{Cl}^{-}
\]

From the weight difference the sulphate content was calculated by the following equation in mg/l.

\[
\text{Sulphate} = \frac{W_1}{V_1}
\]

Where, \(W_1\) = Weight of precipitate in mg/l.

\(V_1\) = Volume of water sample taken.

14. CHLORIDE

Chloride contents were determined by using the argentomertic titration method. The following reactions are involved.

\[
\text{AgNO}_3 + \text{Cl}^{-} \rightarrow \text{AgCl} + \text{NO}_3^{-}
\]

\[
\text{AgNO}_3 + \text{K}_2\text{CrO}_4 \rightarrow \text{AgCrO}_4 + 2\text{KNO}_3
\]

Exactly 25 ml of water sample was taken separately, in a clean dry 250 ml of conical flask. About 3 drops of 10% (W/V) K₂CrO₄ solution was added as an indicator and the end point was reached (permanent reddish tingle colour). From the titre values, the amount of dissolved chloride ions were calculated by using the following formula and given mg/l.

\[
\text{Cl} = \frac{V_2*N*35.45*1000}{V_1}
\]

Where, \(V_1\) = Volume of water sample taken (ml)

\(V_2\) = Volume of AgNO₃ consumed (ml)

\(N\) = Normality of AgNO₃ solution

15. PHOSPHATE

Take a 50 ml of sample diluted to 50ml (V). Add 1ml con. H₂SO₄ and 5 ml con.HNO₃. Digest to 1ml and continue to heating until the solution the solution becomes colorless so that HNO₃ is completely removed. Cool and add 10ml double distilled water. Neutralize with 6N NaOH filter and make upto 50ml. Add 2 ml molybdate reagent and 5 drops of stannous chloride. After 10 minutes but before 12 minutes measure O.D at 690nm(S). Keep this blank for 0 setting of the meter.
Calculation

Phosphate as PO₄ mg/l = [S*Ps*(50/V)]

Present slope (Ps) = 1/Cstd

16. IRON

Take 50ml or a portion of sample diluted to 50ml (V₁) in a 250ml beaker. Add 20ml HNO₃ (1:1). Heat to boiling and reduce the volume to about 10 to 15ml. Add N/8 KMNO₄ and continue boiling till a permanent pink colour is obtained. Cool, make up to 50ml with double distilled water in 50ml Nessler tube. Add 1ml ammonium thiocyanate reagent. If iron is present a red colour is developed. Stir and measure at 470nm (s).

Take 5ml control standard in a 250ml beaker. Add 50 ml double distilled water. Add 2ml HNO₃. Heat to boiling and reduce the volume to about 10 to 15ml. Add N/8 KMNO₄ and continue boiling till permanent pink colour is obtained. Cool and make up to 50ml with double distilled water, in a 50ml Nessler tube.

Calculation

Iron (Fe) mg/l = S*Ps*(50/V₁)

Where, present slope (Ps) = 1/C

17. AMMONIA

Take 100ml sample and add 1.0ml ZnSO₄ solution. Mixed together, with 0.4ml 6N NaOH and allow to stand for few minutes, filter and discard the first 25ml and collect the balance filtrate. From the filtrate take 50ml or a portion diluted to 50ml (V). Add 2 drops of Rochelle salt solution mix, add 1ml Nessler reagent mix allow stand for 10 minutes. Measure optical density at 240nm(s).

Calculation

Ammonia (NH₃) (mg/l) = S*Ps*(50/V)

Where present slope (Ps) = 2/C

18. NITRATE

Take 50 ml of filtered sample. Take 10ml of sample in a boiling tube (V). Place in a cool water bath. Add 2 ml NaCl reagent and 10ml H₂SO₄ reagent. Mix. Allow to cool. Add 0.5 ml Brucine sulphanilic acid. Stir and mix. Keep it in a water bath at 95°C for 20 minutes. Then immense suddenly in a cool water bath. A yellow color develops. Measure the O.D at 410 nm(S).

Calculation

Nitrate as NO₃ (mg/l) = S*Ps*(10/V)

Where, Present slope = 2/C
19. NITRITE

Take 50 ml of dilute sample (V). Add 2 ml color reagent. Mix. Measure O.D(S) at 540nm after 10 minutes but before 2 hours. Take 50 ml distilled water. Add 2 ml color reagent. Use this as blank for 0 setting of the meter.

Calculation

Nitrite as NO₂ mg/l = S*Slope* (50/V)

20. FLUORIDE

Take 100 ml of sample diluted to 100 ml in a Nessler tube (V₁). Add 5 ml Zirconyl Alizarin Reagent. Mix. Keep in the dark for one hour. Note that volume of the standard fluoride with which it is compared (V₂).

Calculation

Fluoride mg/l = (ml standard which compares *10) / (ml, sample used) = (V₂*10)/V₁

21. DISSOLVED OXYGEN

In natural and waste water, DO levels depend on the physical, chemical and biological activities in water body. It indicates the organic pollution in water. The DO contents in water samples were measured by using (Iodometric) Winkler’s method. Exactly 125 ml of water sample was taken separately in a clean, dry 300 ml BOD bottle with a round glass stoppers. 2 ml of Manganese sulphate solution and 2 ml of alkali-iodide azide solution were added without air absorption (the pipette tip should be below the surface layer of water sample). The bottles were closed using stopper without the entrainment of air and the contents were thoroughly mixed by inverting the bottle (20 times) and allowed for 15 mins to settle down the precipitate. The precipitate was completely dissolved and 2 ml of con. H₂SO₄ solution was added through the side wall into each one of the bottles.

The liberated Iodine was titrated against 0.025 N and sodium thiosulphate solution and using 2 %(W/V) starch solution as indicator. The titration is continued until the blue colour disappear. From the titre value the amount of DO was calculated as m/l by using the following equation.

\[ \text{DO} = \frac{(V₂*N*1000*8)}{V₁} \]

Where, \( V₁ \) = Volume of water sample (ml), \( V₂ \) = Volume of sodium thiosulphate (ml), \( N \) = Normality of Na₂S₂O₃ solution.
22. CHROMIUM

Take a sample of 100ml in a 250ml beaker. Add 1 ml of dilute sulphuric acid and two or more acid washed glass beads and heat to boiling. Add 1 drop potassium permanganate solution to give a dark red colour. If fading occurs add potassium for 2 minutes longer. Add 1 ml sodium azide solution and continue boiling gently. If permanganate colour does not fade completely after boiling for approximately 30 seconds, add another 1 ml sodium azide solution. Continue boiling for 1 minute after colour has faded completely and the volume has to be reduced to 10 to 15 ml. Cool and then transfer to 50 ml nessler cylinder and make up to 20 ml with distilled water. Then add 2.5 ml ortho phosphoric acid, 0.5 ml biphenyl carbazide solution and mix well. Wait for 5 to 10 minutes for full colour development and measure the O.D at 540 nm in colorimeter or spectrophotometer.

Calculation

Chromium as Cr mg/l = (O.D for sample *Ps)*(100/Volume of sample)

Present slope (Ps) = 0.05/C std

23. BIOCHEMICAL OXYGEN DEMAND (BOD)

Exactly 10 ml of water sample with 2 ml of (seeding material) domestic waste water was taken in a clean, dry BOD bottle separately and allowed to incubate at 20 °C for 5 days. Further, the BOD measurement procedure was similar to the one carried out for the determination of DO.

\[ \text{BOD} = \left[ (V_1 - V_5) - \left( \frac{X}{X+1} \right) (X+1) \right] \]

Where, \( V_1 \) = Volume (in ml) of 0.025N Sodium thiosulphate for 100 ml of the original solution (1st Day),
\( V_5 \) = Volume (in ml) of 0.025N sodium thiosulphate for 100 ml of incubator solution (5th Day),
\( X \) = Volume of dilution of water (in ml),
\( D \) = Difference between volume of 0.025N sodium thiosulphate required for 100 ml of diluted water before and after incubation (blank correction).

24. CHEMICAL OXYGEN DEMAND (COD)

COD is the measure of oxygen consumed during the oxidation of the oxidisable organic matter by a strong oxidizing agent. \( K_2Cr_2O_7 \) in the presence of sulphuric acid is generally used as an oxidizing agent in determination of COD. Exactly 25 ml of each water sample was taken in a clean, dry 250 ml beaker. About 0.5 gm of mercuric sulphate (Weight of mercuric sulphate added, depend upon the chloride concentration in water) was added and
followed by the addition of 2.5 ml of H$_2$SO$_4$ – AgSO$_4$ solution, 12.5 ml of K$_2$Cr$_2$O$_7$ (0.025N) and 35 ml of H$_2$SO$_4$- AgSO$_4$ solution.

Then, the solution was cooled and boiled for 2 hours in a water bath. Finally the solution was transferred into a 250 ml clean conical flask. 2 drops of feroxin indicator was added and the content were titrated against standard FAS (0.01N) solution until the colour change from bluish green to reddish brown.

From the titre value, COD of water sample was calculated in mg/l.

$$\text{COD} = \frac{(V_2 \times N \times 1000 \times 8)}{V_1}$$

Where, $V_1$ = Volume of water sample (ml), $V_2$ = Volume of FAS consumed by the water sample (ml), $N$ = Normality of FAS solution (0.01N).

**4.3 ANALYSIS OF TANNERY EFFLUENTS**

The data set taken in this study is comprised of 24 parameters (period from October 2010 to March 2011) such as water temperature, pH, Turbidity, TDS, Electrical conductivity, Alkalinity Total as CaCO$_3$, Total hardness as CaCO$_3$ Calcium, Magnesium, Sodium, Potassium, Iron total, free Ammonia, Nitrite, Nitrate, Dissolved oxygen (DO), Total Chromium, Biological oxygen demand, Chemical oxygen demand, Total Suspended Solids, Chloride, Fluoride, Sulphate and Phosphate. These parameters were chosen as they have verified weight factors for different ranges of the parameters to calculate water quality index in various literatures. Collection, stabilization, transportation, storage and analysis of the water quality samples were done in a local laboratory considering the standard methods described in APHA – AWWA$^{15}$ (1998). The physico chemical characteristics of tannery effluents are summarized in table 4.2.
Table 4.2
Physico – Chemical Characteristics of tannery effluents

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<td>Temperature</td>
<td>°C</td>
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<td>26.3</td>
<td>26.2</td>
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<td>6.3</td>
<td>6.38</td>
<td>6.9</td>
<td>7.56</td>
<td>6.8</td>
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<td>NTU</td>
<td>480</td>
<td>455</td>
<td>440</td>
<td>420</td>
<td>410</td>
<td>400</td>
</tr>
<tr>
<td>TDS</td>
<td>Mg/L</td>
<td>27444</td>
<td>26680</td>
<td>25933</td>
<td>18018</td>
<td>10106</td>
<td>10100</td>
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<tr>
<td>Electrical conductivity</td>
<td>µS/cm</td>
<td>40359</td>
<td>39230</td>
<td>38136</td>
<td>26490</td>
<td>14862</td>
<td>14533</td>
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<td>Alkalinity total CaCO₃</td>
<td>Mg/L</td>
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<td>2057</td>
<td>2040</td>
<td>1180</td>
<td>320</td>
<td>308</td>
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<tr>
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<td>Mg/L</td>
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<td>2973</td>
<td>2560</td>
<td>2388</td>
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<td>2372</td>
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<tr>
<td>Calcium</td>
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<td>597</td>
<td>576</td>
<td>533</td>
<td>504</td>
<td>517</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg/L</td>
<td>432</td>
<td>345</td>
<td>269</td>
<td>246</td>
<td>233</td>
<td>241</td>
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<tr>
<td>Sodium</td>
<td>Mg/L</td>
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<td>6120</td>
<td>6200</td>
<td>4062</td>
<td>1950</td>
<td>1900</td>
</tr>
<tr>
<td>Potassium</td>
<td>Mg/L</td>
<td>1600</td>
<td>1435</td>
<td>1280</td>
<td>728</td>
<td>188</td>
<td>179</td>
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<tr>
<td>Iron metal</td>
<td>Mg/L</td>
<td>3.31</td>
<td>3.15</td>
<td>3</td>
<td>3.4</td>
<td>3.83</td>
<td>3.79</td>
</tr>
<tr>
<td>Free Ammonia</td>
<td>Mg/L</td>
<td>1.82</td>
<td>1.8</td>
<td>1.8</td>
<td>1.79</td>
<td>1.8</td>
<td>1.82</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Mg/L</td>
<td>0.31</td>
<td>0.29</td>
<td>0.31</td>
<td>0.3</td>
<td>0.3</td>
<td>0.33</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Mg/L</td>
<td>48</td>
<td>45</td>
<td>48</td>
<td>47</td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>Chloride</td>
<td>Mg/L</td>
<td>11360</td>
<td>11133</td>
<td>10920</td>
<td>7752</td>
<td>4600</td>
<td>4400</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Mg/L</td>
<td>2.4</td>
<td>2.3</td>
<td>2.4</td>
<td>1.7</td>
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<td>1.1</td>
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<td>Sulphate</td>
<td>Mg/L</td>
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<td>1290</td>
<td>1299</td>
<td>903</td>
<td>513</td>
<td>500</td>
</tr>
<tr>
<td>Phosphate</td>
<td>Mg/L</td>
<td>0.45</td>
<td>0.561</td>
<td>0.68</td>
<td>3.46</td>
<td>6.25</td>
<td>6.11</td>
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<tr>
<td>Dissolved oxygen</td>
<td>Mg/L</td>
<td>1.63</td>
<td>1.55</td>
<td>1.51</td>
<td>1.29</td>
<td>1.1</td>
<td>1.13</td>
</tr>
<tr>
<td>Total Chromium</td>
<td>Mg/L</td>
<td>160</td>
<td>154</td>
<td>175</td>
<td>214</td>
<td>233</td>
<td>229</td>
</tr>
<tr>
<td>BOD</td>
<td>Mg/L</td>
<td>2100</td>
<td>2400</td>
<td>2000</td>
<td>3200</td>
<td>214</td>
<td>3000</td>
</tr>
<tr>
<td>COD</td>
<td>Mg/L</td>
<td>4200</td>
<td>4000</td>
<td>4600</td>
<td>5800</td>
<td>5900</td>
<td>6000</td>
</tr>
<tr>
<td>TSS</td>
<td>Mg/L</td>
<td>2281</td>
<td>2200</td>
<td>2189</td>
<td>2500</td>
<td>2100</td>
<td>2198</td>
</tr>
</tbody>
</table>

4.4 WATER QUALITY INDEX (WQI)

Water Quality indices (WQIs) are calculated in two steps. The raw analytical results for the selected water quality variables, having different units of measurements are transformed into unit less sub-index values. This can be done by transforming each

145
parameter into 0 to 100 scale using sub index curves. The sub index curves may be linear, nonsegmented linear and segmented linear\(^1\). These sub indices are then averaged (typically using some type of averaging function) to give a water quality index value\(^1\) applying suitable weighting factors that reflect the importance of each parameters as an indicators of the water quality. The equation for the subjective water quality index \(W_{sub}\) as proposed by Rodriguez de Bassoon\(^9\) (Pesce and Wunderlin\(^2\))

\[
WQI_{sub} = K \frac{\sum_{i=1}^{n} C_i P_i}{\sum_{i=1}^{n} P_i} \quad (1)
\]

Where, \(n\) is the total number of parameters, \(C_i\) is the value assigned to parameter, \(i\) after normalization and \(P_i\) is the relative weight assigned to each parameters. \(P_i\) value range from 1 to 4 , with 4 assigned to a parameter that has the most importance for aquatic life preservation (Dissolved Oxygen) and value of 1 assigned to the parameter that has a smaller impact (Chloride). \(K\) is subjective constant, representing the visual impression of river contamination, the value of which ranges from 0.25 (for highly contaminated water indicated by blackish color, hard, odour and visible fermentation) to (1 for water without apparent contamination, clean or with natural suspended solids). \(W_{sub}\) tends to overestimate the pollution due to the use of a subjective constant, which is not necessarily correlated with the measured parameters. Thus, in this work, such as in other studies reported\(^1\), water quality index was calculated using \(k = 1\) in all the cases to account only for the variations due to measured parameters.

The water quality classification system adopted here is proposed by Kannel\(^2\). According to which, WQI in the range of 0 – 25 is very bad, 26- 50 is bad, 51 – 70 is medium, 71 – 90 is good and 91 – 100 is excellent.

To get the access of water quality using minimum number of parameters\(^9\), used Dissolved Oxygen, Turbidity and Conductivity calculated the minimum water quality index. However, realizing the important parameters as temperature, pH, Dissolved oxygen, Total suspended solids and Electrical conductivity (weights are given equal to each parameter) are used to calculate the minimum water quality index (termed \(WQI_{min}\)) using equation 2. In order to calculate water quality index for all the parameters by using equation 3.

\[
WQI_{min} = K \frac{\sum_{i=1}^{n} C_i P_i}{S} \quad (2)
\]

\[
WQI = k \frac{\sum_{i=1}^{n} C_i P_i}{\sum_{i=1}^{n} P_i} \quad (3)
\]
Normalization factor variables are used in the water quality index calculation and scores of weights are listed in the table 4.3.

**Table 4.3**

Normalization factor Variables used in the water quality index calculation, scores of normalization and relative weights

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Relative weight</th>
<th>Normalization factor (Ci)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p&lt;sub&gt;i&lt;/sub&gt;</td>
<td>100 90 80 70 60 50 40 30 20 10 0</td>
</tr>
<tr>
<td>Wtemp</td>
<td>°C</td>
<td>1 21/16 22/15 24/14 26/12 28/10 30/5 32/0 36/°2 40/°4 45/°6 &gt;45/ &lt;°6</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>pH unit</td>
<td>1 7 7 - 8 7 - 8.5 7 - 9 6.5 - 7 6 - 9.5 5 - 10 4 - 11 3 - 12 2 - 13 1 - 14</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>µS/cm</td>
<td>1 &lt;750 &lt;1000 &lt;1250 &lt;1500 &lt;2000 &lt;2500 &lt;3000 &lt;5000 &lt;8000 &lt;=12000 &gt;12000</td>
<td></td>
</tr>
<tr>
<td>DO</td>
<td>mg/L</td>
<td>4 &gt;=7.5 &gt;7 &gt;6.5 &gt;6 &gt;5 &gt;4 &gt;3.5 &gt;3 &gt;2 &gt;=1 &lt;1</td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>2 &lt;100 &lt;500 &lt;750 &lt;1000 &lt;1500 &lt;2000 &lt;3000 &lt;5000 &lt;10000 &lt;=20000 &gt;20000</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>mg/L</td>
<td>4 &lt;20 &lt;40 &lt;60 &lt;80 &lt;100 &lt;120 &lt;160 &lt;240 &lt;320 &lt;400 &gt;400</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>mg/L</td>
<td>1 &lt;10 &lt;50 &lt;100 &lt;150 &lt;200 &lt;300 &lt;400 &lt;500 &lt;600 &lt;=1000 &gt;1000</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>mg/L</td>
<td>1 &lt;10 &lt;25 &lt;50 &lt;75 &lt;100 &lt;150 &lt;200 &lt;250 &lt;300 &lt;=500 &gt;500</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>mg/L</td>
<td>1 &lt;25 &lt;100 &lt;200 &lt;300 &lt;400 &lt;500 &lt;600 &lt;800 &lt;1000 &lt;=1500 &gt;1500</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>mg/L</td>
<td>1 &lt;25 &lt;50 &lt;100 &lt;150 &lt;200 &lt;300 &lt;500 &lt;700 &lt;1000 &lt;=1500 &gt;1500</td>
<td></td>
</tr>
<tr>
<td>SO₄</td>
<td>mg/L</td>
<td>2 &lt;25 &lt;50 &lt;75 &lt;100 &lt;150 &lt;250 &lt;400 &lt;600 &lt;=1000 &gt;1500</td>
<td></td>
</tr>
<tr>
<td>PO₄</td>
<td>mgP/L</td>
<td>1 &lt;0.025 &lt;0.05 &lt;0.1 &lt;0.2 &lt;0.3 &lt;0.5 &lt;0.75 &lt;1 &lt;1.5 &lt;=2 &gt;2</td>
<td></td>
</tr>
<tr>
<td>NO₃</td>
<td>mgNo₃/L</td>
<td>2 &lt;0.5 &lt;2 &lt;4 &lt;6 &lt;8 &lt;10 &lt;15 &lt;20 &lt;50 &lt;=100 &gt;100</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>mgNo₂/L</td>
<td>2 &lt;0.005 &lt;0.01 &lt;0.03 &lt;0.05 &lt;0.1 &lt;0.15 &lt;0.2 &lt;0.25 &lt;0.5 &lt;=1 &gt;1</td>
<td></td>
</tr>
<tr>
<td>BOD</td>
<td>mg/L</td>
<td>3 &lt;0.5 &lt;2 &lt;3 &lt;4 &lt;5 &lt;6 &lt;8 &lt;10 &lt;12 &lt;=15 &gt;15</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>3 &lt;5 &lt;10 &lt;20 &lt;30 &lt;40 &lt;50 &lt;60 &lt;80 &lt;100 &lt;=150 &gt;150</td>
<td></td>
</tr>
</tbody>
</table>
4.4 a CHEMICAL PARAMETERS RATIO

A few important chemical parameters such as sodium absorption ratio (SAR), percent Sodium (PS), Kelley’s ratio (KR) and Magnesium ratio (MR) are determined to assess the general suitability of the industrial effluent for irrigation. These parameters were calculated by using the following relationships\(^2\).

**Sodium Absorption Ratio (SAR)**

Kelley’s\(^2\) (1951) first pointed out the importance of considering the concentration of Sodium in assessing the suitability of water for irrigation. According to him excess sodium in irrigation water reacts with soil to reduce its permeability as a result of clogging of particles. The parameter that is commonly used to determine whether the amount of sodium in waste water is excessive is the sodium adsorption ratio or SAR\(^2\). This concept is based in equilibrium theory and is defined as

\[
SAR = \frac{Na}{\sqrt{Ca+Mg}}
\]

(4)

Where the concentration of the metal ions are also expressed as milli moles per liter. According to the U.S salinity laboratory, the SAR predicts reasonably well the degree to which irrigation water tends to enter cation exchange reactions in soil. High values for SAR imply a hazard of sodium replacing adsorbed calcium and magnesium, a situation ultimately damaging soil structure.

**Percent Sodium (PS)**

A sodic soil, by definition, contains a high level of sodium relative to the other exchangeable cations (i.e. calcium, magnesium and potassium). A soil is considered "sodic" when the Exchangeable Sodium Percentage (ESP) is 6% or greater. The exchangeable sodium percentage (ESP) is calculated as follows:

\[
\text{Percent sodium PS} = 100\left(\frac{(Na+K)}{(Ca+Mg+Na+k)}\right)
\]

(5)

**Kelley’s Ratio (KR)**

Kelly’s ratio is used to find whether groundwater is suitable for irrigation or not. Sodium measured against calcium and magnesium was considered by Kelly\(^2\) (1951) for calculating Kelly’s ratio. Groundwater having Kelly’s ratio more than one is generally considered as unfit for irrigation.

\[
KR = \frac{Na}{(Ca+Mg)}
\]

(6)
Magnesium Ratio (MR)

Magnesium present in soil and water would adversely affect their quality and render the soil unfit for cultivation\textsuperscript{24}. Magnesium ratio of more than 50\% in a body of water sample will make the water poisonous to plants\textsuperscript{25}.

\[
MR = \frac{100[Mg/(Ca + Mg)]}{(7)}
\]

The amount of sodium relative to total cations is relatively high for the wastewaters compared to the whey because of the use of caustic cleaning chemicals in the factories. This is most pronounced for the Wastewater and it is necessary to add calcium to this system. This has been achieved at some sites by applying lime to the soil. It is also possible to add calcium salt to the wastewater prior to irrigation.

Wilcox Ratio (WR)

Wilcox ratio is determined by

\[
WR = \frac{Na/(Na+Mg+Ca+K)}{(8)}
\]

Where, the ionic Concentration is expressed in milli equivalents per litre. The average values of SAR, PS, KR, MR and WR have been calculated from water quality parameters for the leather tannery effluent.

4.5 EXPERIMENTAL FINDINGS AND ANALYSIS

Data of the physico chemical analysis of leather tannery effluent are found to be very high and well above the permissible limits\textsuperscript{26, 27}. The parameters show the maximum variation in the analyzed samples with respective of their chemical composition. Statistical values are given in the table 4.4.
Table 4.4
Statistical values of water quality parameters of leather tannery effluents

<table>
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<tr>
<th>S.No</th>
<th>Name of the parameters</th>
<th>Units</th>
<th>Mini</th>
<th>Max</th>
<th>Mean</th>
<th>Medium</th>
<th>Std.deviation</th>
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<td>6.7</td>
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<td>NTU</td>
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<td>430</td>
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<td>40359</td>
<td>28935</td>
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<td>1330</td>
<td>1610</td>
<td>1464.25</td>
</tr>
<tr>
<td></td>
<td>of CaCO₃</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Total hardness</td>
<td>Mg/L</td>
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<td>561</td>
<td>554.5</td>
<td>47.84</td>
</tr>
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<td>Mg/L</td>
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<td>432</td>
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<td>1004</td>
<td>535.57</td>
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<tr>
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<td>Sulphate</td>
<td>Mg/L</td>
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<td>1299</td>
<td>966</td>
<td>1096.5</td>
<td>353.29</td>
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<tr>
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<td>3.41</td>
<td>3.355</td>
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<td>Mg/L</td>
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<td>1.82</td>
<td>1.8</td>
<td>1.795</td>
<td>0.0122</td>
</tr>
<tr>
<td>18</td>
<td>Nitrate</td>
<td>Mg/L</td>
<td>45</td>
<td>48</td>
<td>47.5</td>
<td>47.5</td>
<td>1.08</td>
</tr>
<tr>
<td>19</td>
<td>Nitrite</td>
<td>Mg/L</td>
<td>0.29</td>
<td>0.31</td>
<td>0.3</td>
<td>0.305</td>
<td>0.0135</td>
</tr>
<tr>
<td>20</td>
<td>Fluoride</td>
<td>Mg/L</td>
<td>1.1</td>
<td>2.4</td>
<td>1.45</td>
<td>2</td>
<td>0.55</td>
</tr>
<tr>
<td>21</td>
<td>DO</td>
<td>Mg/L</td>
<td>1.1</td>
<td>1.63</td>
<td>1.37</td>
<td>1.4</td>
<td>0.2067</td>
</tr>
<tr>
<td>22</td>
<td>Total chromium</td>
<td>Mg/L</td>
<td>154</td>
<td>233</td>
<td>194</td>
<td>194.5</td>
<td>32.3084</td>
</tr>
<tr>
<td>23</td>
<td>BOD</td>
<td>Mg/L</td>
<td>2000</td>
<td>3200</td>
<td>2600</td>
<td>2650</td>
<td>458.26</td>
</tr>
<tr>
<td>24</td>
<td>COD</td>
<td>Mg/L</td>
<td>4000</td>
<td>6000</td>
<td>5083</td>
<td>5200</td>
<td>837.49</td>
</tr>
</tbody>
</table>
4.5a ANALYSIS OF PHYSICO- CHEMICAL PARAMETERS

1. Colour

Colour in natural water may occur due to the presence of metallic ions such as Iron, Manganese, Suspended matter and industrial waste. Colour due to organic acid may not be harmful as such, but highly coloured. Waters are objected on aesthetic grounds, coloured waters may not be accepted for certain uses in the industries. Several industries use artificial colours such as tannery industries which come out in their waste. The colour of tannery industry is found to be brown in colour.

2. Odour

The Odour may be due to dissolved impurities often organic in nature. It is caused by living and decaying aquatic organism and accumulation of gases like ammonia and hydrogen sulphide. Odours of any artificial origin are due to the discharge of industrial wastes which include many chemicals imparting odour and tastes. Sometimes reagents added to waste supply system may also produce odour.

3. Temperature

The average temperature of leather tannery effluent was 26.95°C and the value of range 26.2-28.3°C. The average value of temperature of the effluent sample is found to be ambient and almost equal to that of room temperature (30°±2°C) observed on the day of sample collection. Hence the effluent is not thermally polluted.

4. pH

The pH of an aquatic system although not definitive is an indicator of the water quality and extent of pollution in the water shed most of the water samples had pH value of between 6.5-7.5. The pH value of effluent fluctuated from 6.3 to 7.56 with an average 6.7 which is within the desirable range 6.5 - 8.5. The effluent from the tannery was found to be slightly acidic with average pH 6.7.

5. Turbidity

Turbidity is a measure of the amount of particulate matter that is suspended in water if normally measured in Nephelometric Turbidity Units (NTU). The value of turbidity range from 400 NTU to 480 NTU and the average turbidity was 434 NTU above the prescribed limit. The water quality parameters such as the turbidity allowed permissible limit 2.5 NTU. It is surprisingly to note that the turbidity of tannery effluent is found to be above the prescribed and desirable limit. The high turbidity may be ascribed to the living and non living suspended matters.
6. Electrical Conductivity

Electrical Conductivity is an excellent indicator of ionic forms of total dissolved salts which is a measure of salinity which affects the taste of portable water\(^{28}\). The tolerance limit of EC is 3000 µS/cm suggested by BIS\(^{29}\) (1983). EC is a function of ion concentration and can be used for a quick checking of dissolved substances in water. The importance of EC is its measure of salinity, which greatly affects the taste and thus has a significant impact on the user’s acceptance of the water as possible. Classification of water based on Electrical Conductivity (EC) is represented in below. The electrical conductivity of the tannery effluent is the range of the 14533 - 40359 µS/cm and the average electrical conductance is found to be 28935 µS/cm which is very much above the permissible limit. It is inferred that tannery effluent lies above permissible level and excessive limit for irrigation. Water quality parameter lies between tolerance limit and excessive limit is given in table 4.5.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Electrical Conductivity in µS/cm</th>
<th>Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;250</td>
<td>Excellent</td>
</tr>
<tr>
<td>2</td>
<td>250 - 750</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>750 - 2250</td>
<td>Permissible</td>
</tr>
<tr>
<td>4</td>
<td>2250 - 5000</td>
<td>Unsuitable</td>
</tr>
</tbody>
</table>

Table 4.5
Classification of water based on Electrical Conductivity

Salinity Hazard

The total concentration of soluble salts (Salinity Hazard) in irrigation water can be expressed in terms of specific conductance (Conductivity) and the samples that fall in the low salinity hazard class (C\(_1\)) can be used for irrigation of most crops and majority of soils. However, some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability. The samples that fall in medium salinity hazard Class (C\(_2\)) can be used if a moderate amount of leaching occurs. High salinity/low sodium water (C\(_4\) and C\(_5\)) can be suitable for plants having good salt tolerance but restricts its suitability for irrigation, especially in soils with restricted drainage\(^{30,31}\). High salinity water (C\(_3\),C\(_4\) and C\(_5\)) cannot be used in soils with restricted drainage. Even with adequate drainage special management /attention for salinity control is required and crops with good salt tolerance
should be selected. It is apparent from the classification on based on salinity hazard (table 4.6) that was found to be excellent (C₁) to good (C₂) for irrigation purpose.

Table 4.6
Salinity Hazard Classes

<table>
<thead>
<tr>
<th>S.No</th>
<th>Salinity Hazard</th>
<th>EC in (µS/cm)</th>
<th>Remark on quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁</td>
<td>100-250</td>
<td>Excellent</td>
</tr>
<tr>
<td>2</td>
<td>C₂</td>
<td>250-750</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>C₃</td>
<td>750-2250</td>
<td>Doubtful</td>
</tr>
<tr>
<td>4</td>
<td>C₄ and C₅</td>
<td>&gt;2250</td>
<td>Unsuitable</td>
</tr>
</tbody>
</table>

7. Total dissolved solids (TDS)

The major part of the TDS is consistent with HCO₃⁻, SO₄²⁻ and chlorides of Ca²⁺, Mg²⁺ and Na⁺. These ions usually comprised about 90% of the TDS. Several hydrochemical processes, which may include movement of ground water through rocks contain soluble mineral materials concentration of water by evaporation and containing of water due to industrial and municipal waste disposals, may cause a use in the dissolved solids. The values of average and range of total dissolved solid are 19713 mg/l and 10100 mg/l - 27444 mg/l. The total dissolved solids are found to be well above the tolerance limit prescribed by BIS²⁹ for the discharge of tannery effluent and hence they are to be necessary to be removed by primary and secondary effluent treatment which before discharging the effluent in order to safeguard the environment. Salinity classification based on total dissolved solids is tabulated below 4.7.

Table 4.7
Salinity classification based on total dissolved solids

<table>
<thead>
<tr>
<th>TDS(mg/L)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1000</td>
<td>Fresh</td>
</tr>
<tr>
<td>1000-3000</td>
<td>Slightly saline</td>
</tr>
<tr>
<td>3000-10000</td>
<td>Moderately saline</td>
</tr>
<tr>
<td>10000-35000</td>
<td>High saline</td>
</tr>
</tbody>
</table>
It is observed that the salinity classification on Total dissolved solids belong to High saline category. Water can be classified based on the concentration of TDS as given in table 4.8.

**Table 4.8**

Classification of water based on concentration of Total Dissolved solids

<table>
<thead>
<tr>
<th>TDS</th>
<th>Water type</th>
</tr>
</thead>
<tbody>
<tr>
<td>up to 500</td>
<td>Desirable for drinking</td>
</tr>
<tr>
<td>500 - 1000</td>
<td>Permissible for drinking</td>
</tr>
<tr>
<td>&lt; 3000</td>
<td>useful for irrigation</td>
</tr>
<tr>
<td>&gt; 3000</td>
<td>Unfit for drinking &amp; irrigation</td>
</tr>
</tbody>
</table>

Total dissolved solids 10,100 mg/l – 27,444 mg/land is more likely to be increased in the tannery effluents. Total dissolved solids during the sampling period are more than the permissible limits and the table clearly showed that tannery effluent is neither useful for irrigation nor allowing them into the land.

8. **Total Suspended solids**

The total Suspended solids of tannery effluent samples are 2100 mg/l to 2500 mg/l which is very above the permissible limit 100 to 600 mg/l.

9. **Alkalinity**

The Alkalinity of the samples is in the range of 308 mg/l -2080 mg/l which is well above the permissible limit 200 mg/l. The effluent samples are having high salinity which is hazardous to human health.

10. **Total hardness**

Total hardness ranged from 2230 mg/l to 3400 mg/l against the permissible limit 500 mg/l. Total hardness as calcium carbonate was noticed comparatively higher. The hardness of water is not a pollution parameter but indicate water quality. Total hardness of tannery effluent samples is found to be extremely hard in all the samples. All the samples are non potable due to higher hardness values by exceeding the permissible limit (600 mg/l) as per standards.

The maximum value of hardness is 3400 mg/l as CaCO₃ at the sample. The ground water of areas which have limestone formations generally have hard water samples collected in the study area is classified as soft or moderately hard. In determining the suitability of
water for domestic and industrial purposes, hardness is also an important criterion as it is responsible for making the water hard. Hence classification of water of the study area based on hardness has been carried and is presented in table 4.9. Accordingly samples collected from tannery industry effluent fall under very hard category.

Table 4.9

Classification based on hardness

<table>
<thead>
<tr>
<th>Hardness as CaCO₃</th>
<th>0-75</th>
<th>75-100</th>
<th>150-300</th>
<th>&gt;300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Soft</td>
<td>Moderate</td>
<td>Hard</td>
<td>Very hard</td>
</tr>
</tbody>
</table>

11. Sodium

Amongst the various cations analyzed sodium content is very high which range from 1900 mg/l to 6200 mg/l and the average sodium found in the tannery effluent was 4388 mg/l which exceeds the desirable limit of 1000-1500 mg/l.

12. Calcium and Magnesium

Calcium contents ranged from 504 mg/l to 640 mg/l which exceeds the desirable limit 50 mg/l. The tannery effluent showed the magnesium content ranged from 233 mg/l to 432 mg/l which is above the prescribed limit 50 to 1 mg/l.

13. Potassium

Similarly Potassium content ranged from 179 mg/l to 1600 mg/l which is above the prescribed limit.

14. Sulphate and Chloride

The values of average and range of sulphate and chloride ion (in mg/l) are 966 mg/l and 500 mg/l to 1299 mg/l and 8360 mg/l and 1360 mg/l to 11133 mg/l respectively. The high content of these ions is responsible for high hardness and it increases the degree of eutrophication.

15. Phosphate

The tannery effluent has more phosphate ion which range from 0.45 mg/l to 6.25 mg/l with an average 2.9 mg/l. Phosphate was noticed comparatively higher. For phosphates, the U.S. Environments protection agency suggested that 0.08 PPM was the critical level for the occurrence of eutrophication in lakes and reservoirs. The amount of phosphate is found out to be much higher than the acceptable limit.

16. Iron

The iron content of all the analyzed samples was found to have 3.41 mg/l concentration which was found to be above the desirable limit of 0.3 mg/l.
17. Free ammonia
The ammonia ranged between 1.79 to 1.82 mg/l which was found to above the limit.

18. Nitrate
Nitrate ranged from 45 mg/l to 48 mg/l which was comparatively higher in the tannery effluent. The raw sewage is the source of nitrate and phosphate in the water. The standard drinking water quality guideline for nitrates is 40 mg/l.

19. Nitrite
It is ranged from 0.29 to 0.31 mg/l which was found to be above the limit.

20. Fluoride
It is observed that the fluoride content in the sample ranged from 1.1 mg/l to 2.4 mg/l, most of which exceed the desirable limited of 1.0 mg/l to the maximum permissible limit of 1.5 mg/l for drinking purpose. It may be inferred that the fluoride was endemic in this area and it is due to the geochemical contamination.

21. Dissolved oxygen
Dissolved oxygen ranged from 1.10 mg/l to 1.63 mg/l in the tannery effluent. Dissolved oxygen depends on physical, chemical and biological activities of the water body. It is very important parameter to check pollution level in water. For drinking water, limit is 6.0 mg/l. Dissolved oxygen is an index of the total organic content of water oxygen demanding substance in water. It means amount of oxygen required for oxidation of oxidizable organic matter.

22. Chromium
The range of chromium level was found to be 154 mg/l to 233 mg/l. It exceeded the permissible limit 0.05 mg/l. They are very high and above the tolerance level. The water from the source needs to be treated before use to avoid its Cagenogenic effect.

23. Biochemical oxygen demand
Biochemical oxygen demand is the measure of the biodegradable organic material present in water sample. The higher values of the BOD have direct correlation with the increase in nutrient level of the lake due to immersion activity. The BOD is directly linked with decomposition of dead organic matter present in the lake and hence the higher values of BOD can be directly correlated with pollution status of the lake. An inverse relation was found between the dissolved oxygen concentration and Biochemical of oxygen demand values. BOD is the amount of oxygen consumed by bacteria in the decomposition of organic material. It also includes the oxygen required for the oxidation of various chemical in the water such as sulphide, ferrous iron and ammonia. BOD ranged from 2100 mg/l to 3200 mg/l.
with an average 2600 mg/l of the tannery effluent which was found to be above the prescribed limit.

24. Chemical oxygen demand

The Chemical oxygen demand is more realistic parameter, which indicates the pollution status of water body as it is related with the allochthonous matter present in the lake. The COD ranged from 4000 mg/l to 6000 mg/l. It was noticed comparatively higher. COD was recorded in the tannery effluent against the prescribed limit 250 mg/l. The COD is used as a measure of the equivalent oxygen of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source COD can be related empirically to BOD organic carbon or organic matter. COD is an index of the total organic content of water oxygen demanding substance in water. It is very high and well above the limit prescribed by BIS standard indicating a heavy load of organic compounds in the industrial effluent. The COD values were found to be much higher than BOD values, indicating considerable presence of chemically oxidizable matter, most of which were non–biodegradable.

The nitrate and phosphate contributed from the use of fertilizer in the agricultural field in river region and it can seep in to the ground water. This reason is comparable with several reports made in literature for contamination of ground water may be due to the seepage of agricultural chemicals, domestic sewage and animal waste. The class of hazard of effluents on the basis of COD is tabulated in table 4.10.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low(mg/l)</th>
<th>Moderate(mg/l)</th>
<th>Severe(mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>&lt;60</td>
<td>60 - 200</td>
<td>&gt;200</td>
</tr>
</tbody>
</table>

It is understood that COD is under severe class. The effluent from tannery industry is not suitable to discharge them into agriculture. The class of hazards of effluent based on the pollutant threshold limit is tabulated in table 4.11.
Table 4.11

Class of hazards of effluents waste water based on limit threshold

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low (mg/lit)</th>
<th>Moderate (mg/lit)</th>
<th>Severe (mg/lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt; 3</td>
<td>3</td>
<td>&gt; 3</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0</td>
<td>50 - 10</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>pH</td>
<td>6 - 6.5</td>
<td>6.5 - 9</td>
<td>&gt; 9</td>
</tr>
<tr>
<td>COD</td>
<td>&lt; 60</td>
<td>6 - 200</td>
<td>&gt; 200</td>
</tr>
</tbody>
</table>

The values of parameters such as Fe, Nitrate, pH and COD of the effluent of leather tannery have been reported in table 4.12.

Table 4.12

Physico chemical parameters and class of hazards of tannery effluent

<table>
<thead>
<tr>
<th>Sampling Period</th>
<th>Fe mg/lit</th>
<th>Class</th>
<th>Nitrate</th>
<th>Class</th>
<th>pH</th>
<th>Class</th>
<th>COD mg/lit</th>
<th>Class of Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct-10</td>
<td>3.31</td>
<td>Severe</td>
<td>48</td>
<td>Moderate</td>
<td>6.36</td>
<td>Low</td>
<td>4200</td>
<td>Severe</td>
</tr>
<tr>
<td>Nov-10</td>
<td>3.158</td>
<td>Severe</td>
<td>45</td>
<td>Moderate</td>
<td>6.3</td>
<td>Low</td>
<td>4000</td>
<td>Severe</td>
</tr>
<tr>
<td>Dec-10</td>
<td>3.0</td>
<td>Moderate</td>
<td>48</td>
<td>Moderate</td>
<td>6.38</td>
<td>Low</td>
<td>4600</td>
<td>Severe</td>
</tr>
<tr>
<td>Jan-11</td>
<td>3.409</td>
<td>Severe</td>
<td>47</td>
<td>Moderate</td>
<td>6.9</td>
<td>Moderate</td>
<td>5800</td>
<td>Severe</td>
</tr>
<tr>
<td>Feb-11</td>
<td>3.83</td>
<td>Severe</td>
<td>48</td>
<td>Moderate</td>
<td>7.56</td>
<td>Moderate</td>
<td>5900</td>
<td>Severe</td>
</tr>
<tr>
<td>Mar-11</td>
<td>3.79</td>
<td>Severe</td>
<td>47</td>
<td>Moderate</td>
<td>6.8</td>
<td>Moderate</td>
<td>6000</td>
<td>Severe</td>
</tr>
</tbody>
</table>

Iron and COD parameters of tannery effluent showed that effluent are in the severe class. The quality of tannery effluent showed that pH and Nitrate are low and moderate class. The quality of waste water is not suitable for irrigation. Variation of the different parameters at different sampling stations along tannery effluents is given in the figures (4.1-4.24).
Variation of the different parameters at different sampling stations along tannery effluents at Dindigul town during study period.

Fig 4.1

Fig 4.2

Fig 4.3

Fig 4.4

Fig 4.5

Fig 4.6

Fig 4.7

Fig 4.8
4.5b RESULTS OF CHEMICAL PARAMETERS

A few important chemical parameters such as Sodium Absorption Ratio (SAR), Percent sodium (PS), Kelley’s ratio (KR), Magnesium ratio (MR) and Wilcox ratio are tabulated in table 4.13.

Table 4.13

Values of SAR, PS, KR, MR and WR of tannery effluents

<table>
<thead>
<tr>
<th>Chemical parameters</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAR</td>
<td>186.30</td>
<td>199.40</td>
<td>213.2</td>
<td>145.53</td>
<td>127.74</td>
<td>69.011</td>
</tr>
<tr>
<td>PS</td>
<td>87.77</td>
<td>88.913</td>
<td>89.849</td>
<td>86.04</td>
<td>74.365</td>
<td>73.282</td>
</tr>
<tr>
<td>KR</td>
<td>5.6902</td>
<td>6.4986</td>
<td>7.337</td>
<td>5.2143</td>
<td>2.645</td>
<td>2.5265</td>
</tr>
<tr>
<td>WR</td>
<td>0.695</td>
<td>0.7203</td>
<td>0.623</td>
<td>0.729</td>
<td>0.6878</td>
<td>0.6697</td>
</tr>
</tbody>
</table>

1. Sodium Absorption Ratio

Sodium absorption ratio is used for adjudicating the irrigation waters. Irrigation waters are classified by Richards\textsuperscript{40} based on SAR. If the SAR is between 0 and 10, the water is excellent and it is good if the value is 10 to 18, the quality is fair if the SAR ranges from 18 to 28, while it is poor beyond 28 based on the above classification. The value of SAR of tannery effluent ranges between 69.011-213.2. It indicates that the effluent is unsuitable for irrigation.

SAR is considered as a better measure of sodium (alkali) hazard in irrigation as SAR of water is directly related to the adsorption of sodium by soil and is a valuable criterion to determine the suitability of the water for irrigation. Excessive sodium content relative to the calcium and magnesium may deteriorate the soil characteristics, thereby reduces the soil permeability and inhibits the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions in a water sample to those of calcium and magnesium. The SAR is used to predict the sodium hazard of high carbonate wasters especially if they contain no residual alkali. The excess sodium or limited calcium and magnesium are elevated by SAR.

2. Percent sodium

Percent sodium value less than 50 are suitable for irrigation\textsuperscript{41} and therefore that tannery effluent has more than 75% sodium. Percent sodium found for tannery effluent was between 73.28-89.25 which are unsuitable for irrigation.
3. Kelley’s ratio

The Kelley’s ratio value is ranged between 2.5265 - 7.337. The KR value for the tannery effluent sample was found to be 4.97 which is more than one and unsuitable for irrigation. Calcium and Magnesium maintain a state of equilibrium generally in most of the water. In equilibrium with more Magnesium being present in water, it will adversely affect the soil quality converting it to alkaline. This inturn affects the crop yields.

4. Magnesium ratio

MR values must be 50% for a water sample for irrigation. Since MR value of the tannery effluent sample is was found to be in the range of 31.58-40.30 which are not suitable for irrigation. But, when the effluents are properly treated, probably they will be more suitable for irrigation.

5. Wilcox ratio

The Wilcox ratio was found to be in the range of 0.623-0.729 which is below the critical value. It is inferred that the amount of sodium present relative to the concentration of other divalent ion present in the tannery effluent is below the critical value. Chemical parameters ratios are shown in figures 4.25 and 4.26.
4.5c ASSESSING THE WATER QUALITY USING WATER QUALITY INDEX (WQI)

Water quality indices appeared in the literature as early as 1965\textsuperscript{42}. The general WQI was developed by Bordalo et al\textsuperscript{43}. WQI is a mathematical instrument used to transform large quantities of water quality data into a single number which provides a simple and understandable tool for managers and decision makers on the quality and possible uses of a given water body. It serves the purpose to improve understanding of water quality status and evaluate water quality trends, to the public and policy makers that are important in terms of increased support for water resources improvement efforts. WQI also permits the assessment of changes in water quality and to identify water trend. Realizing the importance of parameters such as pH, Temp, EC, TSS and DO the minimum water quality index was calculated. It is documented in table 4.14.

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>Oct-10</th>
<th>Nov-10</th>
<th>Dec-10</th>
<th>Jan-11</th>
<th>Feb-11</th>
<th>Mar-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>WQI</td>
<td>30</td>
<td>40</td>
<td>40</td>
<td>36</td>
<td>38</td>
<td>34</td>
</tr>
<tr>
<td>Water class</td>
<td>Bad</td>
<td>Bad</td>
<td>Bad</td>
<td>Bad</td>
<td>Bad</td>
<td>Bad</td>
</tr>
</tbody>
</table>

Table 4.14 clearly showed that WQI characterized the tannery effluent as bad water class. WQI was calculated using all the physico-chemical parameters of leather tannery effluent. It is tabulated in table 4.15. Table 4.15 revealed that leather tannery belonged to the very bad water class.
Table 4.15
Water Quality Index for using all the parameters of leather tannery effluents

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>Oct-10</th>
<th>Nov-10</th>
<th>Dec-10</th>
<th>Jan-11</th>
<th>Feb-11</th>
<th>Mar-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>WQI</td>
<td>10.67</td>
<td>13.0</td>
<td>11.33</td>
<td>12.0</td>
<td>13.33</td>
<td>12.33</td>
</tr>
<tr>
<td>Water class</td>
<td>Very bad</td>
<td>Very bad</td>
<td>Very bad</td>
<td>Very bad</td>
<td>Very bad</td>
<td>Very bad</td>
</tr>
</tbody>
</table>

4.6 CORRELATION AMONG PHYSICO-CHEMICAL PARAMETERS OF LEATHER EFFLUENTS

The correlation co-efficient (r values) for all the possible correlation among water quality parameters are presented in the form of a correlation matrix in Table 4.16. In order to establish the relationship of various physico-chemical parameters, correlation analysis was undertaken. In leather tannery effluent analysis significant positive correlation was observed between different pairs of other parameters such as temperature and Free ammonia (r = 0.84), Temperature and nitrite (r = 0.75). With temperature, other parameters showed Positive and insignificant correlation to one another. The parameter pH is found to have Positive and significant correlation such as pH and Iron (r = 0.81), pH and Phosphate (r = 0.86) pH and Chromium (r = 0.87), pH and BOD (r = 0.71) and pH and COD (r = 0.83). It is interesting to know that pH had significant and negative correlation with pH and Turbidity (r = -0.72), pH and TDS (r = -0.85), pH and EC (r = -0.85), pH and Alkalinity (r = -0.83), pH and Total hardness (r = -0.73), pH and Calcium (r = -0.83), pH and Magnesium (r = -0.766), pH and Sodium (r = -0.85), pH and Potassium (r = -0.85), pH and Fluoride (r = -0.82), pH and SO₄²⁻ (r = -0.85), pH and DO (r = -0.87).

Turbidity has Positive and significant correlation with TDS, EC, Alkalinity, Total hardness, Calcium, Magnesium, Sodium, Potassium, Fluoride, Sulphate and Dissolved oxygen. It is evident from the table that turbidity is due to the presence of dissolved ions. Turbidity has negative and significant correlation with iron, phosphate, chromium, BOD and COD. Total dissolved solids have Positive and significant correlation with EC, Alkalinity, Total hardness, Ca, Mg, Na and chloride. It has negative but significant correlation with iron, NH₃, nitrate and nitrite. Total suspended solids have insignificant Positive and negative correlation with other parameters. Water quality parameters such as electrical conductivity have Positive correlation with Alkalinity, Total hardness, Ca, Mg, Na, K, F, SO₄²⁻ and Dissolved oxygen. It has significant negative correlation with iron, nitrite and PO₄³⁻, Total
chromium, BOD and COD. Alkalinity has Positive correlation with total hardness, Ca, Mg, Na, K, F and Sulphate. It has negative correlation with iron, PO$_4^{3-}$, Cr, BOD, COD and DO. Total hardness has Positive and significant correlation with Ca, Mg, Na, K, F, S and DO but negative significant correlation, Fe, PO$_4^{3-}$, Cr, BOD and COD. Calcium has Positive correlation with Mg, Na, K, NH$_3$, F, SO$_4^{2-}$ and DO, but negative correlation with Iron, phosphate, Cr, BOD and COD. Magnesium has Positive correlation with Na, K, NH$_3$, F, SO$_4^{2-}$ and DO, but negative significant correlation with PO$_4^{3-}$, Cr, BOD and COD. Sodium has positive correlation with K, F, SO$_4^{2-}$ and DO but negative correlation with Iron, PO$_4^{3-}$, Cr, BOD and COD. Potassium has Positive significant correlation with F, SO$_4^{2-}$ and DO but negative correlation with Iron, PO$_4^{3-}$, Cr, BOD and COD. Iron has Positive significant correlation with PO$_4^{3-}$, Cr, BOD and COD, but negative significant correlation with nitrate, Cl, F and DO. Nitrite and nitrate have significant and negative correlation with chloride alone.

Fluoride has significant correlation with sulphate and DO and negative significant correlation with PO$_4^{3-}$, Cr, BOD and COD. Sulphates have Positive significant correlation with DO, but negative significant correlation with PO$_4^{3-}$, Cr, BOD and COD. Phosphate has Positive significant correlation with Cr, BOD and COD and COD and negative significant correlation with DO. Chromium has Positive significant correlation with BOD and COD and negative significant correlation with DO. BOD has Positive significant correlation with COD and negative significant correlation with DO. COD have negative significant correlation with DO. The study revealed that all the physico- chemical parameters are either positively or negatively correlated with each other but significantly.
4.6a CORRELATION BETWEEN COD AND BOD OF TANNERY EFFLUENT

Correlation between COD and BOD of tannery effluents samples has also been evaluated. The waste generated from tannery is highly organic in nature due to high COD and BOD. Correlation between COD and BOD of industrial effluent would be highly advantageous because chemical composition (COD and BOD) is very important deciding factor. In general, the values of COD and BOD are not related since these two tests measure two different characteristics. But on other hand if the quantity and character of the effluents do not change drastically the COD/BOD ratio for polluted water will remain fairly $^{44-48}$. The correlation coefficient between variables X and Y (COD and BOD) was calculated using well known relation.

$$\text{BOD} = b \text{ (COD)} + a \quad ------ \quad (10)$$

The observed COD and BOD values indicate that the values of BOD usually increase in a regular manner with COD. The correlation coefficient ($r$) between COD and BOD of leather tannery effluent was found to be 0.86. It clearly indicates that the probability of definite linear relation exists between BOD and COD.
REFERENCES


38. WQM, Annual report on water quality monitoring of upper and lower lakes Bhopal, (1999), I and II.