

# EVALUATION AND CHARACTERIZATION OF PHYSICO-CHEMICAL PARAMETERS OF TANNERY EFFLUENT

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**Abstract :** Tanneries generate diverse pollution relying upon the technique used. In the present study, the tannery effluent collected from a tannery industry from erode was characterized for fundamental parameters. Tannery effluent became selected and tested for various physical and chemical parameters. The effluent was blackish gray colored with a unpleasant odor and parameters like Alkalinity, Acidity, Temp, pH, Turbidity, with excessive organic and inorganic compounds indicating high Electric Conductivity (EC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total solids (TS), Total Dissolved Solids (TDS), Total Suspended solids (TSS), Total hardness, Oils and Grease. The chemical parameters are Sodium (Na), Potassium (K), Calcium (Ca), Iron (Fe), Chloride (Cl), Nitrite (NO), Nitrate +, Magnesium (Mg), Phosphate, Fluoride, Sulphat and Chromium. The physicochemical parameters were, determined as per the standards prescribed by Bureau of Indian Standards (BIS).

**Keywords:** Effluent, Heavy metals, Tanneries, Physicochemical parameters, Pollution.

## 1. INTRODUCTION

Nature has given gifts like air, water, land, minerals, fossil fuels and numerous sources to man. These gifts have been given to enhance his dwelling standards. But unbridled exploitation regularly resulted inside the release of pollution into the environment (Sarala Thambavani *et al.*, 2009). Pollutants are a major environmental difficulty inside the world due to its damaging impact on residing organism. Inside the beyond few decades, out of control urbanization has caused a extreme pollution problem because of the disposal of sewage and industrial effluents to water our bodies (Tamil selvi *et al.*, 2012). Majority of industries are water based and a full-size extent of waste water emanates from them that's typically discharged into water guides either untreated or inadequately treated inflicting water pollutants (Pandey and Carney, 1998).

Industries together with textiles, engineering, electronics and tannery etc are flourishing in recent years (Islam *et al.*, 1997). The tannery operation consists of converting of the raw cover or skin into leather-based, consequently, make it as a probably pollutants extensive enterprise. Tannery and fabric effluents offer the alteration of physical, chemical and Biological parameters. Tannery is one of the crucial industries inflicting water pollution. Tannery is an oldest and fastest growing industry in India. There are approximately 2161 tanneries in India excluding cottage industries, which processes 500,000 tonnes of hides and skins yearly. A total annual discharge of waste water from those tanneries is 9,420,000 m<sup>3</sup>, which generates about 100,000 m<sup>3</sup> of waste water per day (Mohan *et al.*, 2005) and these industries unfold commonly throughout Tamil Nadu, West Bengal, Uttar Pradesh, Andhra Pradesh, Karnataka, Rajasthan and Punjab (Lefebvre *et al.*, 2005). The effluent generated by using tannery is anticipated at approximately 75,000m<sup>3</sup>/day (Sahasranaman and Buljan, 2000). For processing 7,00,000 tons of hides and skins in line with annum, approximately 4,00,000 tons of chemical compounds are needed. Now not greater than 20% of the chemical compounds are absorbed by way of leather-based; the remainder flows out with the effluent.

In Tamil Nadu, alone there are about 1120 tanneries were focused in Vellore, Ranipet, Tiruchy, Dindugal, Erode and Pallavaram in Chennai. The effluent generated within the tanneries have excessive amounts of natural substances in addition to high attention of chloride, chromium, sulphide and ammonium salts used for the duration

of the manner. Other than the most toxic heavy metals like chromium (Cr) chemical impurities of tannery effluents broadly speaking contains of the following dissolved materials which includes inorganic salt cations (Fe, Zn, Cu, Ca, Na, etc.); anions including SO, NO, PO; and parameters such as DO, TSS, TDS (APHA, 1995). Dyes contributed to overall toxicity at all process stages having high level of BOD, salinity, color, toxicity surfactants, fibers and turbidity and may contain heavy metals (AEPA, 1998; Wynne *et al.*, 2001).

The foremost public situation over tanneries has historically been about odours and water pollutants from untreated discharges. Different problems have arisen greater currently from the increasing use of artificial chemicals together with pesticides, solvents, dyes, finishing marketes and new processing chemical compounds, which introduce problems of toxicity and patience. The present take a look at on the tannery effluent from a tannery enterprise in Erode was aimed to research the characteristics of the effluent as consistent with the standards of BIS, and to study the nature of pollutants present in the effluent.

## 2. MATERIALS AND METHODS

### 2.1 Sample Collection

The effluent was collected from a tannery at Erode, Tamil Nadu, India. The tannery is producing semi-finished tanned leathers. The effluent samples from the raw composite stream were collected in Five-liter containers and were brought to the laboratory with due care.

### 2.2 Physicochemical Characterization of Tannery Effluent

The physicochemical parameters of the effluent were determined as per the standards prescribed by Bureau of Indian Standards (BIS).

#### 2.2.1 Color

Color is measured by visual comparison of the sample.

#### 2.2.2 Odor

The sample was filled half the volume of a wide mouthed stoppered bottle, closed, shake vigorously for 5 seconds, and then quickly observe the odor. The true odor of the sample at the mouth of the bottle was recorded as agreeable or disagreeable.

#### 2.2.3 pH

After calibrating, the instrument with a buffer solution of pH near that of the sample was checked as per the instructions.

#### 2.2.4 Temperature

Temperature measurement is made by taking a portion of the water sample (about 1litre) and immersing the thermometer into it for a sufficient period of time (till the reading stabilizes) and the reading is taken, expressed as °C.

#### 2.2.5 Electrical Conductivity

About 50 ml of standard potassium chloride solution was taken and measured the electrical conductivity at room temperature for calibration. After calibration, 50 ml of the effluent sample was analyzed for the electrical conductivity and expressed as  $\mu\text{s}/\text{Cm}$ .

#### 2.2.6 Total Hardness

To 25 ml of sample in 250ml conical flask, add 25 ml of distilled water, 10 ml of buffer solution and 5 drops of Eriochrome black T. The mixture was titrated against EDTA solution till it turns from wine red to blue. ca equivalent to 1ml of EDTA solution was calculated.

#### 2.2.7 Biological Oxygen Demand

To the sample contained in 300ml BOD bottle, add 2 ml of manganese sulphates solution followed by 2 ml of alkaline iodide solution were added. The content was thoroughly mixed and allowed to precipitate to settle. After settling, the stopper was removed and 2ml of Conc. sulphuric acid was added through the sides. The stopper was replaced and the bottle was shaken thoroughly to dissolve the liberated iodine. 200ml of solution was titrated against sodium thio sulphate solution after adding 3-4 drops of starch indicator. End point is dark blue to colorless. The Procedure was done during 0 h of incubation and after 72 h of incubation.

#### 2.2.8 Chemical Oxygen Demand

Take 50 ml sample in a 250 ml BOD bottles. Add 1 g  $\text{HgSO}_4$  and very slowly add 5ml Sulphuric acid reagent. 25 ml of 0.25 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution was added and mixed. The flask was attached to condenser and turn on cooling water. Add remaining Sulphuric acid reagent (70 ml) to open end of condenser. Continue swirling and

mixing while adding the sulphuric acid reagent. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess  $K_2Cr_2O_7$  with FAS, using ferroin indicator. Although the quantity of ferroin indicator is not critical, use the same volume for all titrations. The first sharp color change from blue green to reddish brown is considered as end point. The blue green may reappear. In the same manner, reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of sample.

### 2.2.9 Determination of Total alkalinity

The alkalinity of sample can be determined by titrating the sample with sulphuric acid or hydrochloric acid of known value of pH, volume and concentrations. Based on stoichiometry of the reaction and number of moles of sulphuric acid or hydrochloric acid needed to reach the end point, the concentration of alkalinity in sample is calculated. A known volume of the sample (50 ml) is taken in a beaker and a pH probe was immersed in the sample. HCl or  $H_2SO_4$  acid (0.1N e.g 8.3 ml conc. HCl in 1000 ml distilled water) added drop by drop until the pH of the sample reached 3.7. The volume of the acid added was noted (Clesceri, 1989).

#### Calculation

Alkalinity as mg/l of  $CaCO_3$  =  $(50000 \times N \text{ of HCl} \times \text{ml acid titrated value}) / \text{volume of sample taken}$

### 2.2.10 Determination of Total acidity

A known volume of the sample (50 ml) is taken in a beaker and a pH probe was immersed in the sample. Sodium hydroxide NaOH (0.1N 4 g NaOH in 1000 ml distilled water) added drop by drop until the pH of the sample reached 8.3. The volume of the NaOH added was noted [Clesceri, 1989].

#### Calculation

Acidity as mg/l of  $CaCO_3$  =  $(50000 \times N \text{ of NaOH} \times \text{ml NaOH titrated value}) / \text{volume of sample taken}$

### 2.2.11 Determination of Total solid

Dry weight of empty dish or crucible (initial weight) add 50 ml sample keep it in water bath until dry keep it in oven (103 to 105°C) for at least 1hour desiccator take final weight of dish (Clesceri, 1989).

#### Calculation

Total solid (mg/l) =  $(\text{final weight} - \text{initial weight}) \times 1000 \times 1000 / \text{volume of sample}$

### 2.2.12 Determination of Total Dissolved Solid

Dry weight of empty dish or crucible (initial weight) take sample and filter with Whatman No.1 add 50 ml filtrate sample keep it in water bath until dry keep it in oven (103 to 105°C) for at least 1hour desiccator take final weight of dish (Clesceri, 1989).

#### Calculation

Total dissolved solid (mg/l) =  $(\text{final weight} - \text{initial weight}) \times 1000 \times 1000 / \text{volume of sample}$

### 2.2.13 Determination of Total Suspended Solid

The difference between the total solids and total dissolved solids is suspended solids.

$$TSS = TS - TDS$$

### 2.2.14 Sulphate

In 100 ml of sample 20 ml of conditioning reagent and a spatula of  $BaCl_2$  were added for 60 sec. The absorbance at 420 nm after 30 sec was noted.

### 2.2.15 Chloride

Standardization of silver nitrate: Pipetted out a 20 ml of standard sodium chloride and transferred into a conical flask and 1 ml of potassium chromate indicator solution was added. Titrated with silver nitrate solution to a pinkish yellow end point.

Analysis of chloride: Took 100ml sample and 1 ml of potassium chromate indicator, titrated with standard silver nitrate solution to obtain a pinkish yellow end point. Parallely, performed a blank titration using water.

### 2.2.16 Phosphates

To 50ml of the filtered sample, 4ml of ammonium molybdate reagent and about 4-5 drops of stannous chloride reagent is added. After about 10 min but before 12 min, the colour developed is measured photometrically at 690nm and calibration curve is prepared. A reagent blank is always run with same treatment with distilled water as sample. The value of phosphate is obtained by comparing absorbance of sample with the standard curve and expressed as mg/L.

*Calculation:*

$$\text{Phosphates (as mg/L)} = \frac{\text{Absorbance of sample} \times \text{Conc. of Std} \times 1000}{\text{Absorbance of Std.} \times \text{Sample taken}}$$

### 2.2.17 Sodium

The filter of the flame photometer is set to 589nm (marked for Sodium, Na). By feeding distilled water the scale is set to zero and maximum using the standard of highest value. A standard curve between concentration and emission is prepared by feeding the standard solutions. The sample is filtered through filter paper and fed into the flame photometer and the concentration is found from graph or by direct readings.

### 2.2.18 Potassium

The filter of the flame photometer is set at 766.5nm (marked for Potassium, K) the flame is adjusted for blue colour. The scale is set to zero and maximum using the highest standard value. A standard curve of different concentration is prepared by feeding the standard solutions. The sample is filtered through the filter paper and fed into the flame photometer. The concentration is found from the standard curve or as direct reading.

### 2.2.19 Calcium

A known volume (50ml) of the sample is pipetted into a clean conical flask, to which 1ml of sodium hydroxide and 1ml of iso-propyl alcohol is added. A pinch of murexide indicator is added to this mixture and titrated against EDTA until the pink colour turns purple.

*Calculation:*

$$\text{Calcium as Ca (mg/L)} = \frac{T \times 400.5 \times 1.05}{\text{Sample taken, ml}}$$

### 2.2.20 Magnesium

Magnesium is a relatively abundant element in the earth's crust, ranking eighth in abundance among the elements. It is found in all natural waters and its source lies in rocks, generally present in lower concentration than calcium. It is also an important element contributing to hardness and a necessary constituent of chlorophyll. Its concentration greater than 125 mg/L can influence cathartic and diuretic actions.

*Calculation:*

$$\text{Magnesium (as mg/L)} = (T - C) \times 0.243$$

where, T = Total hardness mg/L (as CaCO<sub>3</sub>)

C = Calcium hardness mg/L (as CaCO<sub>3</sub>)

### 2.2.21 Nitrates

A known volume (50ml) of the sample is pipetted into a porcelain dish and evaporated to dryness on a hot water bath. 2ml of phenol disulphonic acid is added to dissolve the residue by constant stirring with a glass rod. Concentrated solution of sodium hydroxide or conc. ammonium hydroxide and distilled water is added with stirring to make it alkaline. This is filtered into a Nessler's tube and made up to 50ml with distilled water. The absorbance is read at 410nm using a spectrophotometer after the development of colour. The standard graph is plotted by taking concentration along X-axis and the spectrophotometric readings (absorbance) along Y-axis. The value of nitrate is found by comparing absorbance of sample with the standard curve and expressed in mg/L.

**Calculation:**

$$\text{Nitrates (as mg/L)} = \frac{\text{Absorbance of sample} \times \text{Conc. of Std} \times 1000}{\text{Absorbance of Std.} \times \text{Sample taken}}$$

**3. Result and Discussion**

The physicochemical parameters of the Tannery effluents were analyzed for two samples which has been accrued from Erode district. "the outcomes of the study discovered that color of the untreated Tannery effluent had been blackish with unpleasant odor. This coloration and odor could be due to decomposition of organic and inorganic matters (Singh *et al.*, 1998). The physicochemical traits of the untreated Tannery effluent have discovered that the pH of the Tannery effluent was determined to be alkaline, with excessive BOD, COD, organic particulate matter. The raw effluent became located with dark ash colored, which is probably derived from tanning techniques. Unpleasantly odor can be because of microbial activity increase or the decomposition of organic substance found in it (Goel, 2003; Panneer selvam, 1998). The pH of the tannery effluent changed to be alkaline (7.08 and seven.04) and did no longer meet the overall requirements endorsed via CPCB (1995).

Electrical conductivity is a numerical expression of the ability of water samples to hold an electric cutting-edge. The number depends on the whole concentrations of the ionized substances dissolved in water and to the temperature at which the measurement is made. The conductivity of tannery effluent in the study seems to be very high in Sample A (1243.85  $\mu\text{S/cm}$ ) when compared to Sample B (1065.99  $\mu\text{S/cm}$ ) which can be because of the presence of inorganic substances and salts that display excellent conductivity (Robinson and Stokes, 1959). Rendering with Kataria *et al.*, (1995) high electrical conductivity degree may be because of higher concentration of acid-base and salt in water.

Alkalinity of water is its acid neutralizing capacity. It's miles the sum of all of the bases. The alkalinity of natural water is due to the salt of carbonates, bicarbonates, borates, silicates and phosphates along with hydroxyl ions in the permitted state. Within the tannery effluent under the present study maximum phosphate content (2.58 mg/L in Sample A and 1.96 mg/L in Sample B) was detected in the untreated effluent. However, the primary part of the alkalinity is because of hydroxides, carbonates and bicarbonates (Islam *et al.*, 2014).

**Table 1: Physical Parameters for Tannery Effluent Waste.**

Parameters	Sample A (BP Agragram)	Sample B (Maravapalayam)
Temperature	26.37 $\pm$ 0.12	26.30 $\pm$ 0.26
pH	7.08 $\pm$ 0.01	7.04 $\pm$ 0.01
Colour	Blackish Grey	Grey
Odour	Unpleasant	Unpleasant
Conductivity ( $\mu\text{S/cm}$ )	1243.85 $\pm$ 5.19	1065.99 $\pm$ 1.65
Alkalinity (mg/l)	1223.74 $\pm$ 0.69	1027.44 $\pm$ 0.04
B.O.D (mg/l)	1097.41 $\pm$ 1.60	856.48 $\pm$ 2.00
C.O.D (mg/l)	2771.54 $\pm$ 1.48	2482.83 $\pm$ 3.81
Total hardness (mg/l)	1824.06 $\pm$ 0.92	1693.46 $\pm$ 2.89

Turbidity (NTU)	37.40 ± 0.09	29.30 ± 0.78
D.O (mg/l)	1.65 ± 0.10	3.86 ± 0.03
Acidity	-	-
TS (mg/l)	7666.85 ± 2.47	5576.58 ± 6.84
TSS (mg/l)	2174.69 ± 2.45	2052.48 ± 5.04
TDS (mg/l)	5492.16 ± 0.02	3524.10 ± 3.02
Oil & Grease (mg/l)	0.06 ± 0.01	0.04 ± 0.01

Biological Oxygen Demand (BOD) is one of the chief parameters utilized in water pollution to assess the effect of waste waters on receiving water bodies. The existing have a high stage of BOD (1097.41 mg/L in sample A and 856.48 mg/L in Sample B) in the untreated effluent because of the presence of tremendous quantity of organic matter. Boom in BOD that's a reflection of microbial oxygen demand leads to depletion of Dissolved Oxygen (DO) which may also cause hypoxia conditions with consequent unfavorable consequences on aquatic biota (Jerin, 2011). Chemical oxygen demand (COD) is the finest method for organic matter estimation and rapid test for the resolve of total oxygen demand by organic matter present in the sample. The prevailing research revealed excessive levels of COD (2771.54 mg/L in Sample A and 2482.83 mg/L in Sample B) within the untreated effluent. Improved amount of COD can be because of excessive quantity of organic compounds which are not laid low with the bacterial decomposition (Nagarajan and Ramachandramoorthy, 2002).

Total solids of the untreated effluent were regarding 7666.85 mg/L in sample A and 5576.58 mg/L in Sample B severally that exceeded the permissible limit. These solid impurities cause turbidity within the receiving streams. The composition of solids presents in work effluent in the main depends upon the nature and quality of hides and skins processed within the tannery (Islam et al., 2014). Level of average suspended solids was found to be higher within the effluent when associated to the permissible limit (100 mg/L) prescribed by CPCB (1995) for effluent discharge.

Excessive level of total suspended solids affords in the tannery waste water may be defined to their accumulation during the processing of finished leather-based (Deepa et al., 2011). Somnath (2003) mentioned that large solid particulate be counted stays suspended because of charges on the surface of small debris inside the effluent. Presence of Total suspended solids (TSS) in water ends in turbidity ensuing in bad photosynthetic activity within the aquatic machine (Goel, 2000). In the present study, turbidity of untreated effluent became 37.40 NTU in sample A and 29.30 NTU in sample B.

**Table 2: Chemical Parameters for Tannery Effluent Waste.**

Parameters	Sample A	Sample B
Calcium (mg/l)	314.88 ± 0.45	206.51 ± 0.55
Magnesium (mg/l)	147.19 ± 0.19	123.36 ± 0.36
Sodium (mg/l)	2086.53 ± 1.12	1824.34 ± 1.06
Potassium (mg/l)	317.81 ± 0.55	206.22 ± 0.05

Iron (mg/l)	16.06 ± 0.03	14.33 ± 0.04
Free ammonia (mg/l)	126.13 ± 0.02	107.87 ± 0.03
Nitrate (mg/l)	18.86 ± 0.14	15.82 ± 0.14
Nitrite (mg/l)	1.32 ± 0.02	1.05 ± 0.02
Chloride (mg/l)	1596.14 ± 0.10	1026.45 ± 0.28
Fluoride (mg/l)	2.36 ± 0.02	2.15 ± 0.03
Sulphate (mg/l)	1573.18 ± 1.05	1337.64 ± 0.38
Phosphate (mg/l)	2.58 ± 0.09	1.96 ± 0.02
Chromium (mg/l)	15.06 ± 0.04	13.05 ± 0.03

The turbidity of the effluent is probably due to the discharge of high awareness of carbonates, bicarbonates and chlorides of calcium, magnesium and sodium (Chakrapani, 2005). The composition of solids found in a natural body of water relies upon on the character of the region and the presence of industries close by. Overall dissolved solids of untreated effluent had been located to be 5492.16 mg/L in Sample A and 3524.10 mg/L in Sample B very high compared with Sample B. The value was much greater than the tolerance limits (2100 mg/L) prescribed by Bureau of Indian Standards. Total dissolved solids (TDS) is the degree of total inorganic salts and other substances which might be dissolved in water (Nasrullah et al. 2006). High levels of TDS are aesthetically unsatisfactory and can also produce distress in human and livestock (Patel et al., 2009). Total dissolved solids are specially because of carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, nitrogen, calcium, sodium, potassium and iron (Kannan et al., 2009).

Fluoride content material (2.36 mg/L in Sample A and 2.15 mg/L in Sample B) of the effluent samples were no longer inside the permissible limits (2 mg/L), while the sulphate content of the tannery effluents also exceeding the limit. Sulphate is part of tannery effluent, emanating from using sulphuric acid or products with an excessive (sodium) sulphate content material (Bosnic *et al.*, 2000). Calcium, magnesium, carbonates, bicarbonates, sulphates, chlorides, nitrates, organic matter collectively associate and form hardness of water (Salim et al., 2013).

#### 4. Conclusion:

Tanning is a fundamental part of the method of changing raw hides and skins into completed leather. Tanning is a complex and laborious system that can involve over one hundred thirty special chemicals, relying on the kind of raw fabric used and the completed product. Even though tanning industries are important for the country's economy, their effluent is at once discharged into the nearby water body without treatment. The physicochemical parameters investigated in this study confirmed that the majority the effluent characteristics had been above the provisional discharge restriction. The excessive concentrations of solid substances which includes chloride and sulphate salts as indicated by high total hardness, TDS, BOD, and COD in the tested tannery effluent will affect the quality of water and may cause bad taste and odor. Bioremediation is a choice that offers the opportunity to destroy or render innocent diverse contaminants of tannery effluent by the use of natural biological activity, and therefore, similarly future study is underneath development for the use of greener Bio-method.

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