

A study on the physicochemical characteristics of tannery effluent collected from Chennai

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Abstract - In the present study, the tannery effluent collected from a tannery industry in Chennai was characterized for basic parameters. The effluent was grey colored with a disagreeable odor, acidic in pH, with high organic and inorganic load indicating high Electrical Conductivity (EC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), total hardness, chlorides and sulphates. The physicochemical parameters were determined as per the standards prescribed by Bureau of Indian Standards (BIS).

Key Words: Tannery effluent BOD, COD, TDS

1. INTRODUCTION

Tannery effluent is one of the most polluting industrial wastes. Leather production requires large amount of water - 35 liters of water is consumed per kilogram of raw material processed. The effluent generated by tannery is estimated at about 75,000m³/day (1). For processing 7,00,000 tons of hides and skins per annum, about 4,00,000 tons of chemicals are needed. Not more than 20% of the chemicals are absorbed by leather; the remainder flows out with the effluent.

Effluent from tannery is the most polluting and has high concentration of proteins, chlorides, trivalent chromium, nitrogen, sulphate, sulphides, COD, BOD and suspended solids (2). Volume and characteristics of wastewater discharged vary from process to process, tannery to tannery and from time to time. The operations in a tannery are done in batches and discharge of wastewater is intermittent. Wastewater from beam house operations like soaking, liming, deliming, bathing etc., is alkaline and contains decomposable organic matter, hair, lime, TSS, TDS, sulphides and BOD. This is mainly due to the poor quality of calcium hydroxide and other chemicals used in excess without proper control.

The major public concern over tanneries has traditionally been about odours and water pollution from untreated discharges. Other issues have arisen more recently from the increasing use of synthetic chemicals such as pesticides, solvents, dyes, finishing agents and new processing chemicals, which introduce problems of toxicity and persistence.

The present study on the tannery effluent from a tannery industry in Chennai was aimed to analyse the characteristics of the effluent as per 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 Chennai, Tamil Nadu, India. The tannery is producing semi-finished tanned leathers. The effluent samples from the raw composite stream were collected in a two litre polythene containers and were brought to the laboratory with due care.

2.2 Physico Chemical Characterization of Tannery Effluent

The physicochemical parameters of the effluent such as color, odor, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Hardness, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Sulphates and chlorides were determined as per the standards prescribed by Bureau of Indian Standards (BIS).

Color

Color is measured by visual comparison of the sample.

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.

pH

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

Electrical Conductivity

Reagents:

Standard potassium chloride solution: Dissolve 0.7456 g of anhydrous potassium chloride (0.01N) in distilled water and make up to 1000ml at 25 °C. The specific conductance of this solution at 25°C is 1,408 µs/Cm.

Procedure:

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 µs/Cm.

Total Dissolved Solids

The evaporating dish was heated in an oven at 180°C for one hour, cooled in the desiccators, weighed and stored in the desiccators. A 100 ml of the sample was filtered using pre-weighed Whatmann No.40 filter paper and the weight of the filterable residue was determined. Pipette the 100 ml of sample on to a pre-weighed evaporating dish and placed on a hot air oven. After complete evaporation of water from the residue, the evaporating dish is removed and weighed after cooling in desiccator.

Total Hardness

Principle:

Eriochrome black -T dye when added to water containing calcium and magnesium solution becomes wine red at pH10.0 when this is titrated with EDTA calcium and magnesium will get complexed. At the end of complex formation, solution turns blue from wine red, which is indicated as the end point.

Reagents:

i) Patton and Reeder indicator solution:

1g of Patton and Reeder reagent was dissolved in 100 ml of distilled water EBT indicator: 0.5 g of EBT indicator and 45 g of hydroxylamine hydrochloride were dissolved in 100 ml of spirit.

ii) Standard calcium solution:

0.1 g of CaCO_3 was dissolved in 100 ml of dil HCl (1ml = 0.4008 g of Ca).

iii) Buffer solution:

70 g of Ammonium chloride was added to 570 ml of 30 % ammonium solution in water and make up to 1 liter using distilled water.

iv) 1N Sodium hydroxide:

40 g of NaOH was dissolved in 1 litre of distilled water.

v) 0.001M EDTA solution:

3.75 g of Disodium ethylenediamine Tetra-acetate dihydrate was dissolved in distilled water and make up to 1 liter.

Procedure:

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.

Biological Oxygen Demand

Principle:

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the

specified temperature for 3 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptakes occurring after this measurement is included in the BOD measurement.

Reagents:

i) Manganous sulphate solution:

480g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water, filtered and make up to 1000ml.

ii) Alkaline Iodide Solution:

500g of Sodium hydroxide and 135gm of sodium iodide were dissolved in distilled water and make up to 100ml.

iii) Starch Indicator:

2g of Starch and 0.2g of salicylic acid were dissolved in 100ml of hot water.

iv) Stock sodium thiosulphate solution:

25g of Sodium thiosulphate was dissolved in distilled water and make up to 1000ml 1.0g of sodium hydroxide was added as preservative.

v) Standard sodium thiosulphate solution:

250ml of Stock solution was dissolved in distilled water and make up to 1000ml.

Procedure:

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.

Chemical Oxygen Demand

Principle:

Most type of organic matter is oxidized by a boiling mixture of chromic and sulphuric acids. A sample is refluxed in a strongly acid solution with a known excess of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). After digestion, the remaining unreduced $\text{K}_2\text{Cr}_2\text{O}_7$ is titrated with ferrous ammonium sulphate to determine the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed and the oxidisable matter is calculated in terms of oxygen equivalent.

Reagents:

i) 0.25 N Standard potassium dichromate solution:

12.259 g of $\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved in distilled water and diluted to 1000ml.

ii) Sulphuric acid reagent:

0.55 g of Silver sulphate was dissolved in 100 ml of conc. H_2SO_4 .

iii) Ferroin indicator solution:

1.485 g of 1,10-Phenanthroline monohydrate and 695 mg of $FeSO_4 \cdot 7H_2O$ were dissolved in distilled water and dilute to 100 ml.

iv) 0.25 N Standard Ferrous Ammonium Sulphate (FAS):

98 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was dissolved in distilled water. 20 ml Conc. H_2SO_4 was added, cooled, and diluted to 1000ml. This solution was standardized against standard $K_2Cr_2O_7$.

v) Mercuric sulphate, ($HgSO_4$) and

vi) Potassium hydrogen phthalate (KHP)

Procedure:

Take 50 ml sample in a 250 ml BOD bottles. Add 1 g $HgSO_4$ and very slowly add 5ml sulphuric acid reagent. 25 ml of 0.25 N $K_2Cr_2O_7$ 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 me 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.

Sulphate*Principle:*

Sulfate ion (SO_4^{2-}) precipitated in acetic acid medium with barium chloride to form barium sulphate ($BaSO_4$). Light absorbance of the $BaSO_4$ suspension is determined and the sulphate ion concentration is determined by comparison of the reading with a standard curve.

Reagents:

i) Conditioning reagent 1:

Added a 0.3g of gelatin in 100ml distilled water and warmed it on hot plate till it dissolves. Kept the gelatin solution for about 12 hrs, or overnight preferably at 4 °C. After bringing the solution to room temperature, 3.0g of barium chloride is added to gelatin solution and dissolved by mixing. The turbid solution is kept standing for 2 hrs and mixed before use.

ii) Conditioning reagent 2:

Mixed 50ml glycerol with a solution containing 30ml concentrated hydrochloric acid, 300ml distilled water,

100ml 95%ethyl /isopropyl alcohol and 75g of sodium chloride.

iii) Stock sulphate solution:

Dissolved 0.1479 g anhydrous sodium sulphate in distilled water and make up to 1 litre. (1ml = 0.1 mg SO_4^{2-}).

iv) Standard Sulphate solution:

Prepared a series of standards by diluting the stock solution to cover the range 1 to 40 mg/l (5, 10, 20 and 40 mg/l).

v) Hydrochloric acid (1:9) and, vi) Barium chloride crystals.

Procedure:

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.

Chloride*Principle:*

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated before red silver chromate is formed.

Reagents:

i) Potassium chromate indicator solution:

Dissolved 50 g of Potassium chromate in a little distilled water. Silver nitrate solution was added until a definite red precipitate is formed. Let it stand for 12 hours, filter and dilute to 1 liter with distilled water.

ii) 0.014 N Standard silver nitrate:

Dissolved 2.395 g of silver nitrate in distilled water and diluted to 1 litre.

iii) 0.0141 N Standard sodium chloride solution:

Dissolved 824.0 mg of sodium chloride in distilled water and diluted to 1 litre.

iv) Aluminum hydroxide suspension:

Dissolved 1.25 g of aluminum potassium sulphate in 1 litre of distilled water.

Procedure:

Standardisation 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.

3. RESULTS AND DISCUSSIONS

3.1 Physicochemical Characterization of Leather Effluent

The physicochemical characteristics of the untreated tannery effluent have revealed that it is acidic, with high BOD, COD, organic particulate matter, unpleasant odour and colour. The raw effluent was observed with dark ash coloured, which might be derived from tanning processes. Unpleasant odour may be due to microbial growth or the decomposition of organic substance present in it (3, 4). The pH of the tannery effluent was highly acidic (5.8 to 6.6) and did not meet the general standards recommended by CPCB (1995) for the discharge of effluents into land or irrigational purpose. Discharge of such untreated effluents with such a low pH into ponds, rivers or on lands for have direct impact over zooplankton and fishes, since low pH level may affect the physiology of fishes (5).

Electrical conductivity is a numerical expression of the ability of water sample to carry an electric current. The number depends on the total concentrations of the ionised substances dissolved in water and to the temperature at which the measurement is made. The conductivity of tannery effluent in the present study was found to be very high which may be due to the presence of inorganic substances and salts that show good conductivity (6). According to Kataria *et al.*, (7) high electrical conductivity level may be due to higher concentration of acid-base and salt in water.

Table -1: List of methods used for physicochemical characterization

S. No.	Characteristics	Methods
1	Color	IS 3025: Part 4-2000
2	Odor	IS 3025: Part 5-1983 (Reaffirmed 2006)
3	pH	IS 3025: Part 11-1983 (Reaffirmed 2006)
4	EC	IS 3025: Part 14-2001
5	TDS	IS 3025: Part 16-1984 (Reaffirmed 2006)
6	BOD	IS 3025: Part 44-1993 (Reaffirmed 2009)
7	COD	APHA 21 st Ed., 2005. Section 5220 B, 5-14
8	Total hardness	IS 3025: Part 21-1999.
9	Sulphates	IS: 3025: Part 24-1986
10	Chlorides	IS 3025: 2 Part 32-1988 (Reaffirmed 2009)

High level of total suspended solids present in the tannery effluent could be attributed to their accumulation during the processing of finished leather. Moreover, presence of total suspended solids leads to turbidity resulting in poor penetration of light in the aquatic system, thereby affects the photosynthetic activity (3). Further the settling of suspended

particles on soil and soil fauna, might lead to various damages like change in soil porosity, soil texture, water holding capacity on one hand (8) and clogging of gills and respiratory surfaces of fishes on the other hand (9).

Biochemical Oxygen Demand is one of the important parameters used in water pollution studies to evaluate the impact of wastewaters on receiving waters. The present study has revealed the high levels of biological oxygen demand in the tannery effluents (793 mg/l) indicating high organic load. Present investigation is in agreement with the studies on tannery effluent (10), sugar mill effluent, sago effluent (4) and distillery effluent (11). According to Poole *et al.* (12), increase in BOD is a reflection of microbial oxygen demand, which leads to depletion of dissolved oxygen. Under such a condition, no aquatic life can survive, except anaerobic microorganisms. Further, the presence of organic matter will promote anaerobic action leading to the accumulation of toxic compounds in water bodies (3)

Chemical Oxygen Demand is the best method for the determination of total oxygen demand by organic material present in the effluent. In the present investigation, high level of COD was recorded (2479 mg/L) which did not meet the standard prescribed by CPCB (1995) for effluent discharge into inland surface water (permissible limit: 250 mg/l). This indicates that the effluent is unsuitable for the existence of the aquatic organisms. Raj *et al.* (13) recorded higher values of COD for the treated tannery effluent of a tannery industry in Chrompet, Chennai.

Ions, especially calcium, sulphate, magnesium and sodium impart hardness to water. The results revealed that the concentrations of ions were more than the prescribed limit by CPCB (1000 mg/L). According to Lehr *et al.* (14), the water is very hard if the value is beyond 180 mg/L. In the present study, the value ranges near 2870 mg/L, which indicated that the water hardness was very high.

Table -2: Physicochemical characterization of raw tannery effluent

S.No.	Characteristics	Units	Observations
1	Color	-	Grey
2	Odor	-	Disagreeable
3	pH	-	0.8
4	EC	µS/cm	12659
5	TDS	mg/L	3059
6	BOD	mg/L	895
7	COD	mg/L	2381
8	Total Hardness	mg/L	1460
9	Chlorides	mg/L	1592
10	Sulphates	mg/L	1338

High levels of chlorides in the tannery effluent could be attributed to the soaking process involved (15). More over high content of ions, hardness present in the tannery effluent might be due to mixing of tannery effluents with the aqueous system from the different sources of processing within the tannery.

The results of the present investigation revealed the acidic pH, increased total hardness, high TDS, BOD, and COD of the tannery effluent. The present study also revealed that, the tannery effluent was highly polluted and do not satisfy the prescribed limits of the CPCB (1995). Hence, it is imperative to adopt technologies that could reduce or degrade the tannery effluent effectively. According to McEldowney et al. (16), the most appropriate method for pollution control depends on various factors linked to the nature and type of pollution with environmental statutes, cost benefit analysis and commodity acceptance, Since no single technology can satisfy all these requirements, combined treatment strategies could be an option.

4. CONCLUSIONS

Tanning is an integral part of the process of converting raw hides and skins into finished leather. Tanning is a complicated and laborious process that can involve over 130 different chemicals, depending on the type of raw material used and the finished product. In most developing countries, tannery effluents are discharged into sewers or inland surface waters and/or brought onto the land with irrigation water. The high concentrations of solid substances such as 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.

Discharge of untreated tannery effluents into the sewer system causes deposition of calcium carbonate and choking of the sewer. Hence, a better approach than the traditional methods is to destroy the pollutants if possible, or at least to transform them to innocuous substances is necessary. Bioremediation is an option that offers the possibility to destroy or render harmless various contaminants of tannery effluent using natural biological activity, and therefore, further study is under progress using greener biomethod.

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