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Evaluation and Characterization of Tannery Wastewater

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Abstract— **The leather industry is suffering from the negative impact generated by the pollution it causes to the environment. Nearly 70% of the pollution loads of BOD, COD, and Total Dissolved Solids (TDS) are generated from soaking, liming, degreasing, pickling and tanning processes. There is an enormous pressure from the various pollution control bodies to regulate and minimize the amount of pollution generated from the leather processing. The need for use of alternative to chemical methods to combat pollution problem have become necessary to protect the industry and to comply with the environmental norms. In the present study, effluent samples were collected from a tannery in Khartoum -Sudan. The effluent samples were collected from the all stages of processing viz., soaking, liming, deliming, pickling, Chrome tanning and Retanning. The physicochemical parameters of the tannery effluent viz., pH, alkalinity, acidity, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), suspended solids (SS), chlorides and sulfides were determined. All the parameters included in this study are found to be higher than the prescribed discharge limits for tannery industries. The investigation of the tannery wastewater from different tanning processes gave a number of conclusions. The results indicate that the wastewaters from the tanneries do not satisfy the legal ranges of selected parameters discharge to inland water and to sewer.**

Index Terms — **Alkalinity, Acidity, COD, BOD, Tannery wastewater, Sulfides, Chlorides**

I. INTRODUCTION

The tanning process aims to transform skins in stable and imputrescible products namely leather. There are four major groups of sub-processes required to make finished leather: beamhouse operation, tanyard processes, retanning and finishing **[1,2,3]**. However for each end product, the tanning process is different and the kind and amount of waste produced may vary in a wide range **[2, 4]**. Traditionally most of tannery industries process all kind of leathers, thus starting from dehairing to retanning processes. However in some cases only pre-pickled leather is processed with a retanning process.

Acids, alkalis, chromium salts, tannins, solvents, sulfides, dyes, auxiliaries, and many others compounds which are used in the transformation of raw or semi-pickled skins into commercial goods, are not completely fixed by skins and remain in the effluent. For instance the present commercial chrome tanning method gives rise to only about 50–70% chromium uptake **[5]**. During retanning procedures, synthetic tannins (Syntan), oils and resins are added to form softer leather at varying doses **[6]**. One of the refractory groups of chemicals in tannery effluents derives mainly from tannins **[7]**. Syntans are characterized by complex chemical structures, because they are composed of an extended set of chemicals such as phenol-, naphthalene-, formaldehyde- and melamine-based syntans, and acrylic resins **[8, 9, 10]** . Among syntans, the ones based on sulfonated naphthalenes and their formaldehyde condensates play a primary role, for volumes and quantity used in leather tanning industry **[10]**. The oils cover the greater COD equivalents compared to the resins and syntans. The BOD_5/COD ratio of syntans was also lower than other compounds **[9]**.

A brief description about the wastes generated from a tannery and their impact on the environment would be appropriate to understand the problem associated with it (**Fig. 1**). The beam house operations soaking, liming and deliming lead to discharge of high amount of sulfides, lime, and ammonium salts, chlorides, sulphate, and protein in the effluent. Consequently, the wastewater is characterized with high amount of BOD and COD. Soak liquor contains, suspended solids, dirt, dung, blood adhering to hides and skins, and chloride etc. lime liquors are highly alkaline. This stream contains suspended solids, dissolved lime, sodium sulfide, high ammoniacal nitrogen and organic matter. Unhairing and fleshing effluent contains fatty fleshing matter in suspension. The spent deliming liquors carry significant BOD load. The spent bate liquors on account of presence of soluble skin proteins and ammonium salts containing high organic matter. Pickle liquors are acidic and contain high amount of salt. The spent chrome liquors contain high concentration of chrome compounds and neutral salts. The wastewater from neutralization, retanning, dyeing and fatliquoring sections contribute little pollution load **[11]**. Solvents and this leads to the emission of volatile organic compounds (VOC) **[12]**.

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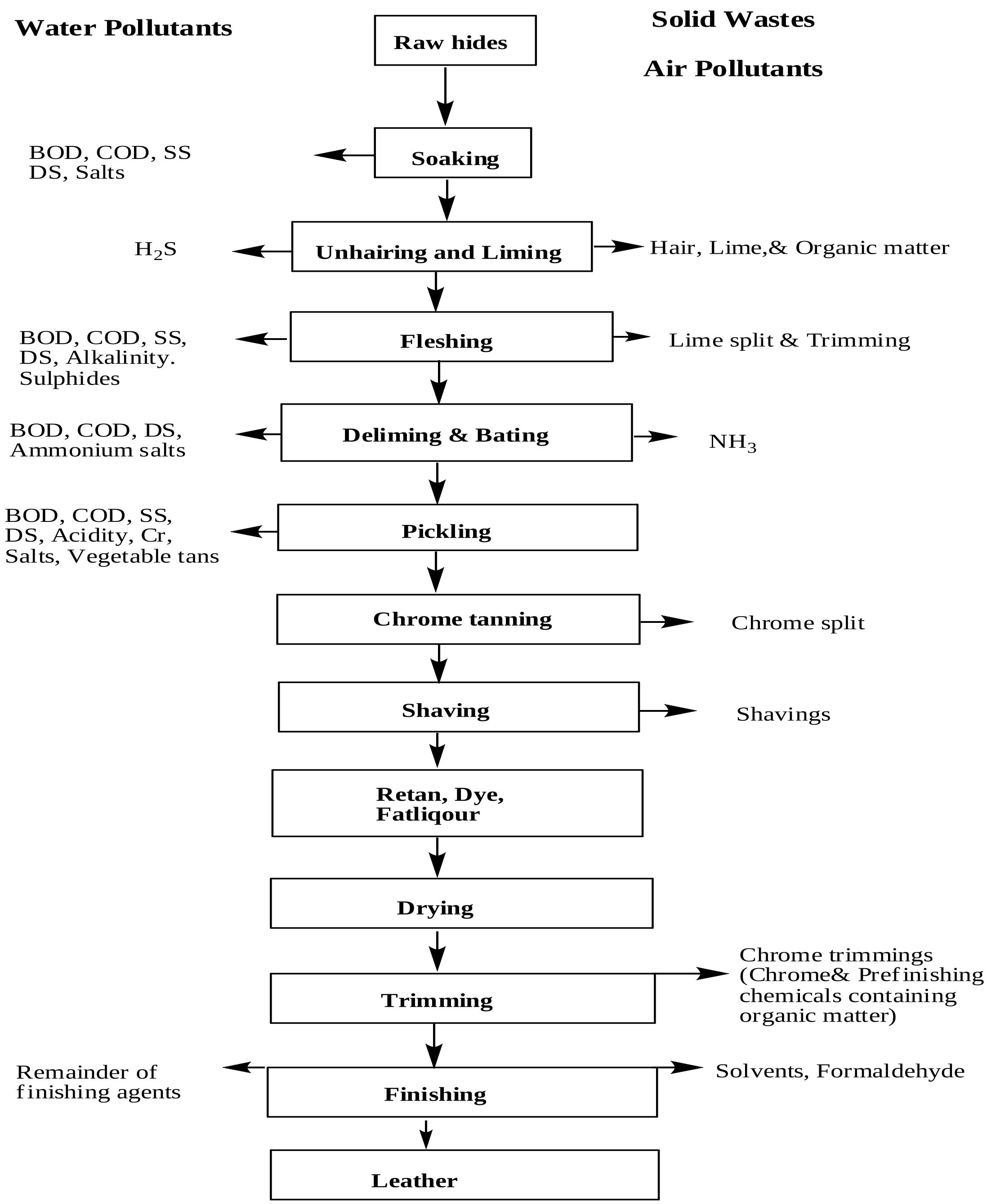

Figure 1: Wastes generated from each unit operation of a tannery

An average of 30–35 m^3 of wastewater is produced per ton of raw hide. However, wastewater production varies in wide range (10–100 m^3 per ton hide) depending on the raw material, the finishing product and the production processes [2]. Organic pollutants (proteic and lipidic components) are originated from skins (it is calculated that the raw skin has 30% loss of organic material during the working cycle) or they are introduced during processes. The parameters of tannery effluent were found to be high and exceeding the legal ranges of selected parameters discharge to inland water and to sewer (**Table 1**) [13].

Table 1
Legal ranges of selected parameters

Parameter	Direct discharge to inland water	Discharge to sewer
pH	5.0-10.0	5.0-10.0
Temperature (^oC)	25-40	30-40
Settl. Solids (mg/l)	0.3-1.0	
BOD_5 (mg/l)	5-200	125-1000
COD (mg/l)	50-450	300-3000
SS (mg/l)	20-200	75-1000
Sulfide (mg/l)	Nil-10.0	Nil-10.0
Cr III	0.1-5.0	1.0-10
Cr VI (mg/l)	Nilhil-1.0	Nilhil-1.0
Oil & grease (mg/l)	2.5-100	30-500
Phenols (mg/l)	0.05-5.0	1.0-90
Chlorides (mg/l)	200-4000	400-600
Sulfates (mg/l)	150-1000	300-400
TKN (mg/l)	3-10	

The difficulty in treatment of tannery wastewater is due to complex nature of the industry and a large number of chemicals employed in the leather processing. The segregation of each sectional stream and separate treatment therefore requires very high investments in terms of equipment, land etc. hence eliminating or reducing the wastage at the source i.e. at the stage of leather processing, is a promising option for the tanneries. Some of cleaner technological options are discussed in **Table 2 [14].**

Table 2
Cleaner Technological Options and its Advantages

Cleaner technology option	Impact on pollution load
Salt free hide and skin preservation	Helps eliminate salt and reduce TDS
Mechanical desalting	Helps eliminate salt and reduce TDS
Counter current soaking	Reduced water consumption
Enzyme assisted soaking	Reduced water consumption and processing time
Green fleshing	Reduced chemical consumption and solid waste
Enzymatic sulfide free unhairing	Reduced concentration of sulfides, COD, etc in the effluent
Liming splitting	Reduced chemical consumption and solid waste
Hair saving unhairing-liming	Reduced concentration of nitrogen, BOD, COD etc in effluent
Direct recycling of liming floats	Reduced chemical and water consumption and reduced BOD, COD and sulfides in effluent
Ammonia free deliming using carbon dioxide	Reduced nitrogen concentration in the effluent
Chrome recovery, high chrome exhaustion and/or chrome liquor recycle	Reduce concentration of chromium in the effluent

The objectives of this study to correlate chemical properties of polluted water discharged from tannery, viz., pH, chloride, sulfide, BOD_5, COD, alkalinity, acidity, T.S.S, TDS and assessment of tannery wastewater in the different tanning processes viz. soaking, liming and unhairing, deliming and bating, pickling, tanning and retanning processes.

II. MATERIALS AND METHODS

Materials

For the present study, effluent samples were collected from a tannery in Khartoum- Sudan. The effluent samples were collected from the all stages of tanning processing viz., soaking, liming, deliming, pickling, Chrome tanning and Retanning. The effluent was collected in polythene containers of $2\frac{1}{2}$ litres capacity and were brought to the laboratory with due care and was stored at 20^oC for further analysis. Chemicals used for the analysis of spent liquor were analytical grade reagents. The physical and chemical characteristics of tannery effluents parameters viz. pH, total alkalinity, total acidity, , COD, BOD_5, total solids (TS), total dissolved (TDS), total suspended solids (TSS), chlorides and sulfides were analysed as per standard procedures [15].

Methods

Determination of pH

The pH is determined by measurement of the electromotive force (emf) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode (usually a calomel electrode). Contact is achieved by means of a liquid junction, which forms a part of the reference electrode. The emf of this cell is measured with pH meter.

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 [15].

Calculation

Alkalinity as mg/l of $CaCO_3$ =

(50000× N of HCl× ml acid titrated value)/volume of sample taken

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 [15].

Calculation

Acidity as mg/l of $CaCO_3$ =

(50000× N of NaOH × ml NaOH titrated value)/volume of sample taken

Determination of chemical oxygen demand (COD)

The chemical oxygen demand of an effluent means the quantity of oxygen, in milligram, required to oxidize or stabilize the oxidizable chemicals present in one litre of effluent under specific condition. 2.5 ml of the sample was taken in tube, 1.5 ml of 0.25 N $K_2Cr_2O_7$ (potassium dichromate),spatula of mercuric sulphate $HgSO_4$ and 3.5 ml of COD acid were added and kept in COD reactor for 2 hrs at 150^oC. After cooling the sample titrated against FAS (standard ferrous ammonium sulfate 0.1N) and used ferrion as indicator. The end point is reddish brown color. In the blank tube 2.5 ml of distilled water was taken and then follow the same procedure in the sample [15].

Calculation

COD (mg/l) = (blank value-titrated value) ×N of FAS×8000/ volume of sample

8000 = mill equivalent wt of O_2×1000ml

Determination of biochemical oxygen demand (BOD)

Biochemical oxygen demand (BOD) of an effluent is the milligram of oxygen required to biologically stabilize one liter of that effluent (by bio-degradation of organic compounds with the help of micro-organisms) in 5 days at 20^oC.If the BOD value of an effluent is high, is high, then that effluent contains too much of bio-degradable organic compounds and so will pollute the receiving water highly.

Procedure

1. Take 5 litres of distilled water → aerated for 3.5 hours → added nutrients 1 ml nutrient for 1 litre aerated distilled water (FeCl, CaCl2, PO4, MgSO4, domestic water) → aeration for 30 minutes.

2. BOD bottle (300 ml) → add sample → fill the bottle with aerated water → put the lid (avoid air bubbles) → keeping BOD incubator at 20^oC for 5 days → after 5 days take the bottle and add 2 ml $MnSO_4$, 2 ml alkali azide iodide and 2 ml conc. H_2SO_4. → shake the bottle well (yellow colour) → take 200 ml sample → add starch solution as indicator (purple colour) → titrated with 0.025 N sodium thiosulphate → end point colour change from purple to colorless. In blank filled the bottle with aerated water without the sample and follow the procedure [15].

Calculation

BOD_5 = (blank value-titrated value) ×300/volume of sample

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Determination of Total solid

The term 'solid' refers to the matter either filtrable or non-filtrable that remains as residue upon evaporation and subsequent drying at a defined temperature. Residue left after the evaporation and subsequent drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include "Total suspected solids" (TSS) and "Total dissolved solids" (TDS).

Procedure

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 1 hour → desiccator → take final weight of dish **[15]**.

Calculation

Total solid (mg/l) = (final weight-initial weight) ×1000×1000 / volume of sample

Determination of total dissolved solid

Procedure

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 1 hour → desiccator → take final weight of dish **[15]**.

Calculation

Total dissolved solid (mg/l) =

(final weight-initial weight) ×1000×1000 / volume of sample

Determination of total suspended solid

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

TSS = TS-TDS

Determination of chloride

Chloride is determined in a natural or slightly alkaline solution by titration with standard silver nitrate, using potassium chromate as an indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed.

Procedure

Take sample (10 ml to 50 ml) → add 2 ml of hydrogen peroxide (H_2O_2) → add 2 ml K_2CrO_4 (potassium chromate indicator) → titrate with silver nitrate (0.0141 N) → end point formation of reddish yellow colour (yellow to orange). In blank trial take distilled water instead of sample and follow the same procedure above **[15]**.

Calculation

Chloride (mg/l) = (A-B) ×N. of silver nitrate×35.45×1000/ volume of sample

A = ml titration for sample

B = ml titration for blank

N = normality of $AgNO_3$

Determination of sulfide

The sulfides in the solution are oxidized with and excess of a standard iodine solution and the excess back titrated with a standard thiosulfate solution.

Procedure

Take sample (10ml) in conical flask → add 5 ml zinc acetate(5%) → filter through filter paper → take the filter paper and put it in the same conical flask → add 100 ml distilled water. → then add 20 ml iodine solution and 4 ml 6N HCl → add 2 drops of starch as indicator (puple colour will form) → titrate against sodium thiosulphate (0.025N) → end point the colour change from blue colour to colourless. In the blank test take 100 ml distilled water instead of sample and follow the same procedure above for the sample **[15].**

Calculation

$$\text{Sulfide (mg/l)} = \frac{(BV - TV) \times N.thio \times 400}{volume of sample \times N.iodine}$$

BV= blank value

TV= titrated value

III. RESULTS AND DISCUSSION

Characteristics of tannery wastewater

Wastewater of each tannery process consists of pollution of varying pH values. Similarly a large variation exists in every parameter BOD, COD, Chloride, Sulphate, etc. Discharge of these chemicals into wastewater is hazardous for the environment. Analysis of physical and chemical characteristics of the tannery wastewater collected from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling, chrome tanning and retanning are shown in **Table 3.**

Table 3
Analysis of tannery wastewater

Parameter	Soaking	Liming & Unhairing	Deliming & Bating	Pickling	Chrome Tanning	Retanning
pH	7.50	12.50	8.80	2.8	3.50	4.5
Total Alkalinity	2500±500	17500±500	12000±500	-	-	-
Total Acidity	-	-	-	3500±100	2500±100	2000±100
BOD 5 DAY @20oC (total)	1850±50	7500±150	2500±120	600±50	650±50	1450±50
COD (Total)	4600±150	18600±150	6300±150	1550±50	1700±50	3650±50
Total solids (TS)	45000±1500	36000±1500	9000±500	52000±1500	46000±1500	12000±1500
Total Dissolved Solids (TDS)	36500±1500	25000±1500	5800±500	49500±1500	44000±1500	10500±1500
Suspended solids (SS)	8500±500	9000±500	3200±500	2500±500	2000±500	1500±500
Chlorides as Cl	19250±1500	-	-	23500±1500	-	-
Sulfides as S	-	380±50	-	-	-	-

All values except pH are expressed in mg/l

Determination of pH

The pH of the tannery wastewater from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling , chrome tanning and retanning is given in **Table 4.1** and did not meet the general standards recommended **[13]** for the discharge of wastewater into inland surface water of for irrigation purposes. Discharge of untreated effluents with such a pH into ponds, rivers or on lands for any purpose may be detrimental to soil fauna and aquatic biota such as zooplankton and fishes, since low pH level may affect the physiology of fish.

Determination of Biochemical Oxygen Demand (BOD)

BOD is measure of the content of organic substances in the waste water which are biologically degradable with consumption of oxygen. Usually indicated as 5-day biochemical oxygen demand (BOD). This is the amount of oxygen in milligrams per litre (mg O_2/l) that consumed by microorganisms in 5 days at 20^oC for oxidation of the biologically degradable substances contained in the water. The results of present study revealed that BOD level from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling , chrome tanning and retanning is given in **Fig. 2** and indicating high organic load surpassed legal limit of (5-200) mg/L of effluent discharge into inland surface waters **[13]**. The presence of organic matter will promote anaerobic action leading to the accumulation of toxic compounds in the water bodies. Present result is in agreement with the studies on tannery effluent **[16]**. From the **Fig. 2** high level of BOD found in the liming and unhairing process.

Determination of Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is quantity of oxygen expressed in milligram consumed by the oxidisable matter contained in one litre of the sample. The test is performed by vigorous oxidation with chemicals and back-titrating the chemical consumed for oxidation. COD is system of measuring the content of organic impurities with oxidizing agents. The results of present study revealed that COD level from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling, chrome tanning and retanning is given in **Fig. 3** and it exceed the permissible COD level of (50-450) mg/L **[13]**, this indicates that the effluent is unsuitable for the existence of the aquatic organisms, due to the reduction in the dissolved content.

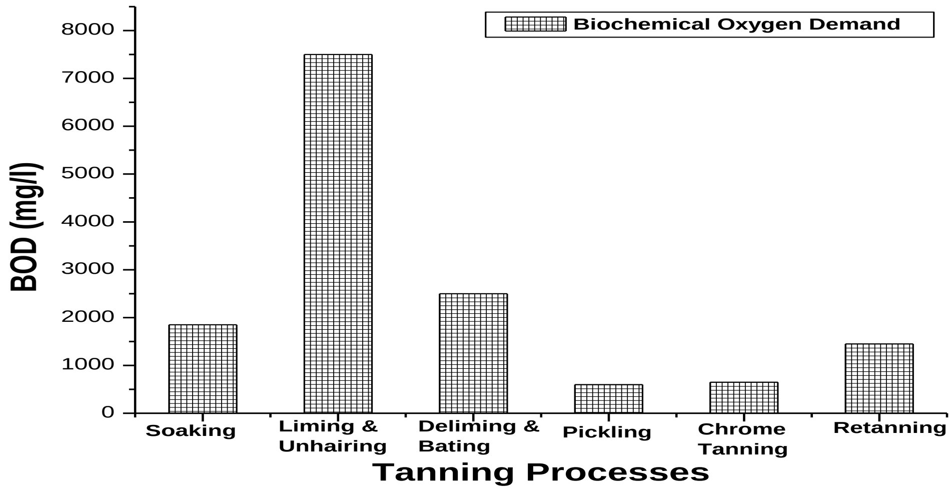

Figure: 2 Graphical representation of biochemical oxygen demand in different tanning processes

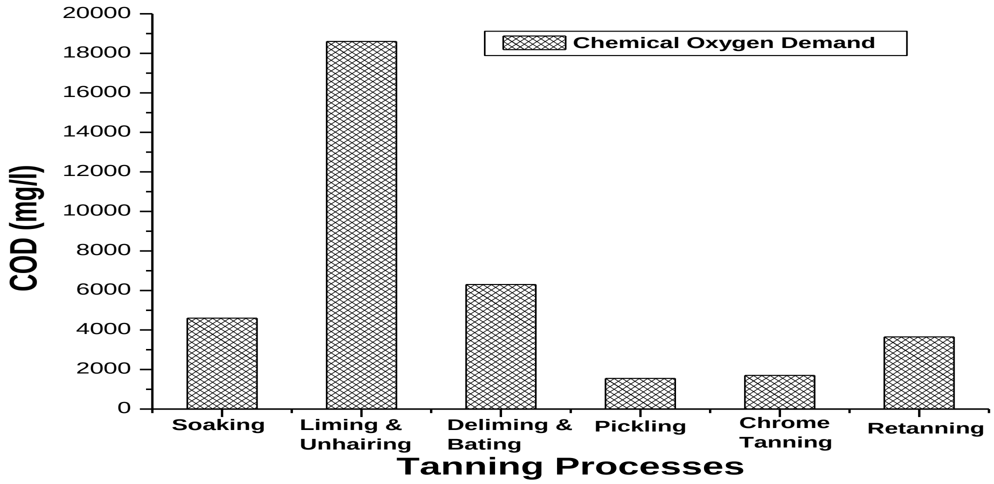

Figure: 3 Graphical representation of chemical oxygen demand in different tanning processes

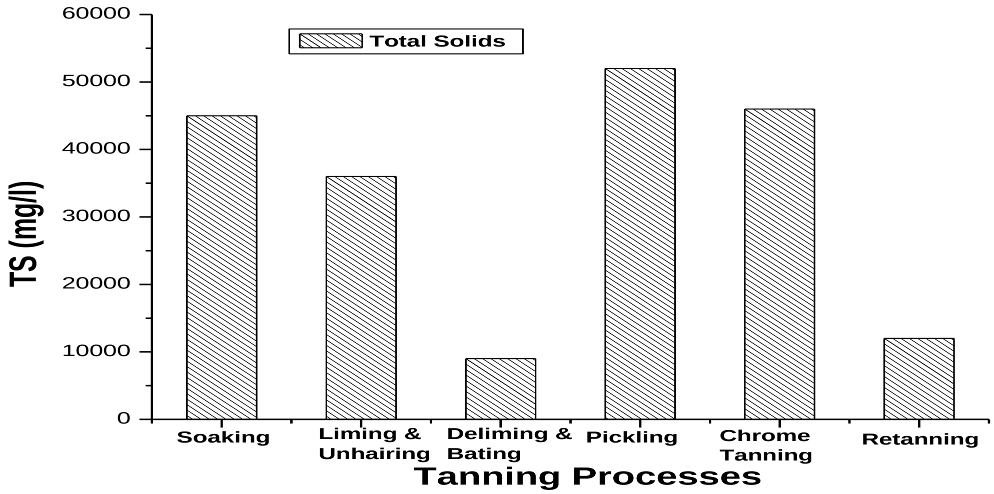

Figure: 4 Graphical representation of total solids in different tanningprocesses

Determination of Total Solids (TS)

The results of present study revealed that TS level from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling , chrome tanning and retanning is given in **Fig. 4** and it exceed the permissible TS level of 110 mg/L. These solid impurities cause turbidity in the receiving streams. The composition of solids present in tannery effluent mainly depends upon the nature and quality of hides and skins processed in the tannery.

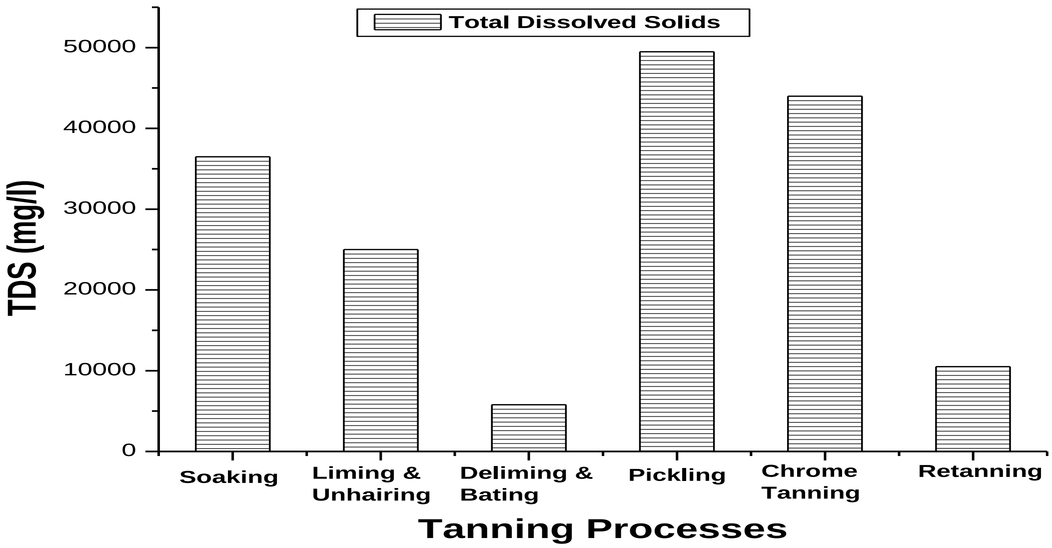

Figure: 5 Graphical representation of total dissolved solids in different tanning processes

Determination of Total Suspended Solids (TSS)

The results of present study revealed that TSS level from different tanning processes viz. soaking, liming and unhairing, deliming and bating pickling , chrome tanning and retanning is given in **Fig. 6** and it exceed the permissible TSS level of (20-200) mg/L. These suspended impurities cause turbidity in the receiving streams. The composition of solids present in tannery effluent mainly depends upon the nature and quality of hides and skins processed in the tannery. High level of total suspended solids present in the tannery effluent could be attributed to their accumulation during the processing of finished leather. Presence of total suspended solids in water leads to turbidity resulting in poor photosynthetic activity in the aquatic system **[18]** and clogging of gills and respiratory surfaces of fishes **[19]**.

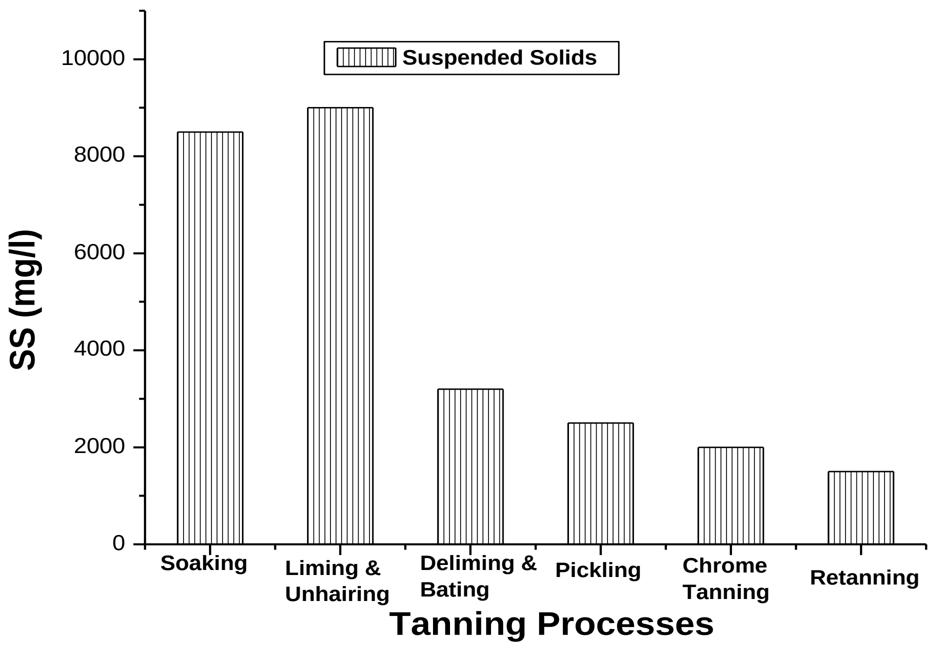

Figure: 6 Graphical representations of suspended solids in different tanning processes

Determination of Chloride

The results of present study revealed that chloride level from soaking and pickling, are 19250 mg/l, 23500 mg/l respectively (**Table 3**) and the levels exceed the permissible chloride level of 1000 mg/L of effluent discharge into inland surface waters. High levels of chlorides in the tannery effluent could be attributed to the soaking and pickling processes. The chloride content in water sample gives an idea of the salinity of water sample.

Determination of Sulfide

Sulfides are particularly objectionable because hydrogen sulfide will be liberated if they are exposed to a low pH environmental, and if they are discharged into stream containing iron, black precipitates will be formed. Sulfides may be toxic to stream organisms or to organisms employed in biological treatment systems. The results of present study revealed that sulfide level from liming and unhairing process is given in **Table 3** and it exceed the permissible sulfide level of 2 mg/L. of effluent discharge into inland surface waters**[13]**.

Determination of Total Alkalinity

Alkalinity of water is its acid neutralizing capacity. It is the sum of all 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 Free State. However the major portion of the alkalinity is due to hydroxides, carbonates and bicarbonates. The results of present study revealed that alkalinity level from soaking, liming and unhairing, and deliming & bating process is given in **Table 3.**

Determination of Total Acidity

Acidity of water is measured by hydrogen ion concentration, usually called pH. Waters with pH below 7.0 are acid. In unpolluted water, acidity comes from dissolved carbon dioxide or organic acids leached from the soil. Atmospheric pollution also may cause acidity. Acid waters can corrode metal or concrete. The results of present study revealed that acidity level from pickling, chrome tanning, and retanning is given in **Table 3.**

IV. CONCLUSIONS

The processing of hides and skins into leather is carried out in an aqueous medium and hence the discharged water from pits, drums or paddles containing several solubles and insolubles constitutes the effluents from the tannery. In the present study, investigation of the tannery wastewater from different tanning processes gave a number of conclusions. Results of the analysis showed that the tannery wastewater from different tanning processes viz., soaking, liming and unhairing, declaiming and bating, pickling, chrome tanning and retanning is highly with a disagreeable pH, alkalinity, acidity, total solids, total dissolved solids, suspended solid, chemical oxygen demand, biochemical oxygen demand, chlorides and sulfides. The results of the analysis indicate that the wastewaters from different units of the tannery do not satisfy the legal ranges of selected parameters.

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