

# PEER REVIEW ON SEWAGE TREATMENT OF TANNERY INDUSTRIES

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**Abstract** - The industrial sector is one of the main sectors that contribute to the growth of the country. Thus the emission of wastewater from the growing industries also increases which leads to various problems. Hence treatment of this wastewater is essential. There are various processes involved in the treatment of wastewater. Industrial processed water must be of an appropriate quality to ensure that products comply with required quality standards and that the manufacturing process is both efficient and controllable. Industrial wastewater treatment covers the mechanisms and processes used to treat wastewater that is produced as a by-product of industrial or commercial activities. After treatment the treated effluent is sent again to industries for future and continuous processes. The water is recycled and used.

**Key words:** *By-product, Emission, Industrial treatment, Wastewater.*

## 1. INTRODUCTION

Sewage is a type of wastewater that is produced from a community of people. It is characterized by volume or rate of flow, physical condition, chemical and toxic constituents, and its bacteriologic status. It consists mostly of greywater (from sinks, tubs, showers, dishwashers, and clothes washers), blackwater (the water used to flush toilets, combined with the human waste that it flushes away); soaps and detergents; and toilet paper (less so in regions where bidets are widely used instead of paper). Whether it also contains surface runoff depends on the design of sewer system. Sewage treatment is the process of removing contaminants from wastewater, primarily from household sewage. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safer treated wastewater (or treated effluent). A by-product of sewage treatment is usually a semi-solid waste or slurry, called sewage sludge, that has to undergo further treatment before being suitable for disposal or land application.

Sewage is generated by residential, institutional, commercial and industrial establishments. In many areas, sewage also includes liquid waste from industry and commerce. The separation and draining of household waste into grey water and black water is becoming more common in the developed world, with treated greywater being permitted to be used for watering plants or recycled for flushing toilets.

### 1.1 Sewage mixing with rainwater

Sewage may include storm water runoff or urban runoff. Sewerage systems capable of handling storm water are known as combined sewer systems. This design was common when urban sewerage systems were first developed, in the late 19th and early 20th centuries. Combined sewers require much larger and more expensive treatment facilities than sanitary sewers. Heavy volumes of storm runoff may overwhelm the sewage treatment system, causing a spill or overflow. Sanitary sewers are typically much smaller than combined sewers, and they are not designed to transport storm water. Backups of raw sewage can occur if excessive infiltration/inflow (dilution by storm water and/or groundwater) is allowed into a sanitary sewer system. Communities that have urbanized in the mid-20th century or later generally have built separate systems for sewage (sanitary sewers) and storm water, because precipitation causes widely varying flows, reducing sewage treatment plant efficiency.<sup>[3]</sup>

As rainfall travels over roofs and the ground, it may pick up various contaminants including soil particles and other sediment, heavy metals, organic compounds, animal waste, and oil and grease. Some jurisdictions require storm water to receive some level of treatment before being discharged directly into waterways. Examples of treatment processes used for storm water include retention basins, wetlands, buried vaults with various kinds of media filters, and vortex separators (to remove coarse solids)

### 1.2 Industrial effluent

In highly regulated developed countries, industrial effluent usually receives at least pre-treatment if not full treatment at the factories themselves to reduce the pollutant load, before discharge to the sewer. This process is called industrial wastewater treatment or pre-treatment. The same does not apply to many developing countries where industrial effluent is more likely to enter the sewer if it exists, or even the receiving water body, without pre-treatment.

Industrial wastewater may contain pollutants which cannot be removed by conventional sewage treatment. Also, variable flow of industrial waste associated with production cycles may upset the population dynamics of biological treatment units, such as the activated sludge process.

Tanning industry is one of the oldest industries in the world. It is typically characterized as pollutants generated industries which produce wide varieties of high strength toxic chemicals. It is recognized as a serious environmental threat due to high chemical levels including salinity, organic load (chemical oxygen load or demand, biological oxygen demand), inorganic matter, dissolved, suspended solids, ammonia, total kjeldahl nitrogen (TKN), specific pollutants (sulfide, chromium, chloride, sodium and other salt residues) and heavy metals etc. Large quantity of water is used in tanning process of which 90% of the water is discharged as effluent. A part of the leather processing, solid and gaseous wastes are also discharged into the environment. During the chrome tanning process, 40% unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment. Exposure to chromium, pentachlorophenol and other toxic pollutants increase the risk of dermatitis, ulcer nasal septum perforation and lung cancer. Without any exceptions there is no effluents treatment plant (ETP) in leather tanning industries in the country and moreover, the owners of tannery industries are not much concerned about human health and environmental safety.

The high concentrations of pollutants with low biodegradability in tannery wastewater represent a serious and actual technological and environmental challenge. Thus, the leather industry is being pressured to search cleaner, economically as well as environmentally sustainable wastewater treatment technologies. 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: beam house operation, tan yard processes, retanning and finishing. However for each end product, the tanning process is different and the kind and amount of waste produced may vary in a wide range. 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. fig 1 shows the Sources and types of pollutants generated in leather processing. Wastes originate from all stages of leather making, such as fine leather particles, residues, from various chemical discharges and reagents from different waste liquors comprising of large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags.

Tanning refers to the process by which collagen fibres in a hide react with a chemical agent (tannin, alum or other

chemicals). However, the term leather tanning also commonly refers to the entire leather-making process. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep and pigs.

Out of 1000 kg of raw hide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of raw material is converted into leather. A typical tannery generates huge amount of waste.

- Fleshing – 56% - 60%
- Chrome shaving, chrome splits and buffing dust – 35% - 40%
- Skin trimming – 5% - 7%
- Hair – 2% -5%

Over 80% of the organic pollution load in BOD terms emanates from the beam house (pre-tanning), much of this comes from degraded hide/skin and hair matter. During the tanning process at least 300 kg of chemicals (lime, salt etc) are added per tonne of hides. Excess of non-used salts will appear in the wastewater.

Because of the changing pH, these compounds can participate and contribute to the amount of solid waste or suspended solids. Every tanning process step, with the exception of finishing operations, produces wastewater. An average of 35m<sup>3</sup> is produced per tonne of rawhide. The wastewater is made up of high concentration of salts, chromium, ammonia, dye and solvent chemicals etc.

A large amount of waste generated by tanneries is discharged in natural water bodies directly or indirectly through two open drains without any treatment. The water in the low lying areas in developing countries, like India and Bangladesh, is polluted in such a degree that it has become unsuitable for public use. In summer when the rate of decomposition of the waste is higher, serious air pollution is caused in residential areas by producing intolerable obnoxious odours. Tannery wastewater and solid wastes often find their way into surface water, where toxins are carried downstream and contaminate water used for bathing, cooking, swimming and irrigation. Chromium waste can also seep into the soil and contaminate groundwater systems that provide drinking water for nearby communities. In addition, contamination in water can build up in aquatic animals, which are a common source of food.

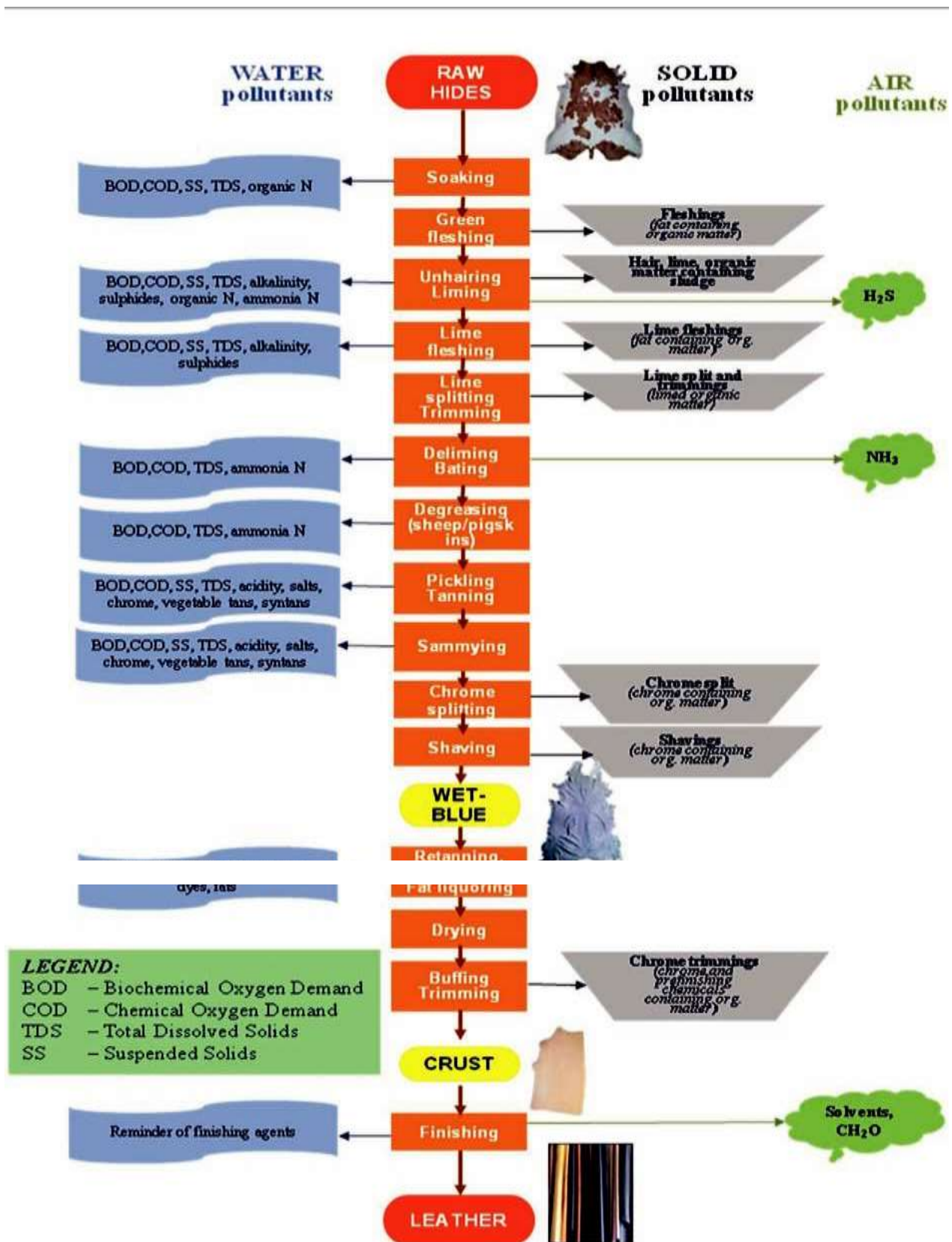


Fig 1. Sources and types of pollutants generated in tannery industries



### 1.3 TREATMENT

Wastewater treatment is a multi-stage process to purify wastewater before it enters a body of natural water, or it is applied to the land, or it is reused. The goal is to reduce or remove organic matter, solids, nutrients, Cr and other pollutants since each receiving body of water can only receive certain amounts of pollutants without suffering degradation. Therefore, each effluent treatment plant must adhere to discharge standards limits usually promulgated by the relevant environmental authority as allowable levels of pollutants, for practical reasons expressed as BOD<sub>5</sub>, COD, suspended solids (SS), Cr, total dissolved solids (TDS) and others. The three main categories of tannery wastewater, each one having very distinctive characteristics, are:

- Effluents emanating from the beam-house – liming, delimiting/bating, water from fleshing and splitting machines; they contain sulphides, their pH is high, but they are chrome-free.
- Effluents emanating from the tan yard (tanning and re-tanning, sammying) – high Cr content, acidic.
- Soaking and other general effluents, mainly from post-tanning operations (fat-liquoring, dyeing) – low Cr content.

The tannery segregates effluents from beam house and tankard as well as from retaining and finishing operations. The effluents are then collected in sumps and fine screened to remove coarse solids. The sulphide bearing liquors from liming and the subsequent washes are collected and oxidised applying Jet ox Venturi aeration. The effluents are combined and mixed in an aerated balancing tank using submerged Jet ox venture mixing. The balancing allows for a uniform flow to the flocculator of the dissolved air floatation, where aluminium sulphate and a polymer product are added to facilitate coagulation and flocculation of the solids. The solids are then floated in the DAF unit and removed by an automatic scraper. The sludge is pumped to a sludge holding tank and then dewatered using a high-pressure belt press. The afore mentioned primary treatment removes an average of 95% of suspended solids (SS) and 70%-80% of COD, which is a significant improvement on the usual 80%-90% SS and 50%-65% COD removal achieved with sedimentation.

Effluent segregation and screening tannery effluents contain many types of pollutants which are present in all forms from large solids through colloids to dissolved salts. The flow and composition of the effluent also varies considerably during the day and from the various stages of the tanning process. Pre-treatment is especially important in the treatment of tannery wastewater to remove coarse solids and to equalise flow variations in order to protect and optimise the subsequent processes. Particles, which can be easily abstracted by physical and/or mechanical

means, are usually removed from the liquid effluent at the earliest possible stage. This prevents problems of blockage and weir on pumps, pipe work and other subsequent treatment equipment.

The catalytic oxidation by aeration of lime liquor is the most economical and widely used process for sulphide removal. The technique consists of aerating the spent lime liquors for 5 to 8 hours in the presence of a catalyst such as manganese sulphate. The sodium sulphide present in the spent and unhairing and liming liquors is oxidized by the air oxygen into thiosulphate and in smaller quantities into sulphate. The thiosulphate then decomposes into sulphur and sulphite. Depending on the length of the float used and the volume of wash and rinse waters, the lime liquors may contain between 2.5-8g/lit of sulphide. After mixing and dilution with rest of the tannery effluent, the sodium sulphide concentration is between 200-600 mg/lit. Therefore, it is required to separately treat the unhairing liming floats before they are mixed with other effluent streams. Common discharge limits to a municipal sewer may range from 0.5-10 mg/lit (as S<sub>2</sub>). For most locations, whereas typical sulphide levels in the untreated effluent is of the order of several hundreds. Usually 2-5ppm of residual sulphides can be expected in such plants. Consequently 0 ppm H<sub>2</sub>S was detected with a draeger around the whole effluent treatment plant.

It is necessary to balance effluents to improve the treatment efficiency and to avoid oversize treatment plants, which have to deal with peak effluent flows. In addition to flow balancing, the equalization tank provides for neutralization and precipitation. It is necessary to provide effective mixing and aeration to achieve equalization, prevent anaerobic conditions and settle the suspended solids.

#### 1.3.1 Preliminary treatment

Typically, in the case of common effluent treatment plants (CETPs) servicing tannery clusters often found in developing countries, it is essential to have pre-treatment units installed in individual tanneries. Their role is to remove large particles, sand/grit and grease, but also to significantly reduce the content of chrome and sulphides before the effluent is discharged into the collection network.

#### 1.3.2 Physical-chemical treatment (primary)

Primary treatment of sewage by quiescent settling allows separation of floating material and heavy solids from liquid waste. The remaining liquid usually contains less than half of the original solids content and approximately two-thirds of the BOD in the form of colloids and dissolved organic compounds. Where nearby water bodies can rapidly dilute this liquid waste, primary treated sewage may be discharged so natural biological decomposition oxidizes remaining waste. The objective

here is the removal of settle able organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25-50% of the incoming bio-chemical oxygen demand (BOD<sub>5</sub>), 50-70% of total suspended solids (SS), and 65% of the oil and grease are removed during primary treatment. The effluent and sludge from primary sedimentation are referred to as primary effluent and sludge.

Primary sedimentation is a physical and chemical separation which leads to settlement of suspended solids and colloidal substances. Sedimentation occurs, when the velocity of effluent is reduced below the point at which it can transport the suspended solids matter. The suspended solids settle and can be removed as sludge. The physical removal of the suspended solids and colloidal substances from the wastewater is enhanced by chemical conditioning of the wastewater. The effluent is pre-treated by dosing of a coagulant, such as alum or ferric salts, followed by polyelectrolyte flocculants which aid the phase separation. The dosing of these chemical conditioners requires prior pH adjustment of the feed streams for optimum chemical dosage. Modern tannery effluent treatment plants apply mainly dissolved air floatation, which is the most efficient method of removing suspended solids. The main advantages are less space requirements and better performance compared with settlements techniques. Dissolved air floatation works on the reverse principle to sedimentation, employing fine air bubbles to lift suspended solids to the surface. This leads to the formation of a floating sludge layer, which is removed with a scraper. The main advantage is that fine solids such as hair and fibres or fats and proteins can also be very efficiently removed by floatation. Air dissolved under pressure in a saturator with part of the recycled treated/effluent. When the pressure is subsequently relieved in the floatation vessel, small air bubbles rise on the surface, carrying the suspended solids. A scraping device periodically removes the surface sludge.

The floatation process relies on coagulant and flocculant chemical conditioning of the feed stream in order to enhance the solid separation process. A suitable coagulant is in-line dosed to the effluent, followed by pH adjustment and polymer addition. The suitable polymer is required for optimum phase separation, especially of colloidal solids. After chemical dosing the effluent flows into the floatation tank and is mixed with the rising air bubble stream. The air saturated stream is formed by pumping of the treated effluent into a pressurisation chamber along with air, which under pressure, dissolves in the water. The sudden release of pressure in the floatation tank causes the dissolved air to form "clouds" of tiny air bubbles which come up to the surface carrying the suspended and colloidal solids with them to form a surface scum or sludge layer which is regularly scraped off.

### 1.3.3 Biological treatment (secondary)

Secondary treatment is a treatment process of waste water (or sewage) to achieve a certain degree of effluent quality by using a sewage treatment plant with physical phase separation to remove settleable solids and a biological process to remove dissolved and suspended organic compounds. After this kind of treatment, the wastewater may be called as secondary-treated wastewater.

In most cases, secondary treatment follows primary treatment, its goal being the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is carried out in the presence of oxygen by aerobic micro-organisms (principally bacteria) that metabolize the organic matter in the wastewater, thereby producing more micro-organisms and inorganic end products (principally CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O). Several aerobic biological processes are used for secondary treatment and the differences among them have to do primarily with the manner in which oxygen is supplied to the micro-organisms and with the rate at which organisms metabolize the organic matter

### 1.3.4 Advanced (tertiary) treatment:

The purpose of the tertiary treatment is to provide a final treatment stage to raise the effluent quality to the desired level. This advanced treatment can be accomplished by a variety of methods such as coagulation, sedimentation, filtration, reverse osmosis, and extending secondary biological treatment to further stabilize oxygen-demanding substances to remove nutrients. In various combinations, these processes can achieve any degree of pollution control desired. As wastewater is purified to higher and higher degrees by such advanced treatment processes, the treated effluent can then be reused for urban, landscape and agricultural irrigation, industrial cooling and processing, recreational uses and water recharge, and even indirect and direct augmentation of drinking water supplies. Tertiary or advanced wastewater treatment is employed to reduce residual COD load and/or when specific wastewater constituents are not removed by previous treatment stages.

### 1.3.5 Sludge handling and disposal

Effluent treatment plants produce treated, "cleaned" effluent and sludge because inherently the primary aim of wastewater treatment is the removal of solids and some potentially hazardous substances from the wastewater. Furthermore, biologically degradable organic substances are converted into bacterial cells, and the latter are removed from the wastewater. The wastewater produced during tanning activities are commonly conveyed to centralised industrial wastewater treatment plants. Sludge from physical-chemical treatments and waste activated sludge from biological

treatment units are called tannery sludge. Tannery sludge is a solid waste that needs to be carefully managed and its disposal represents one of the major problems in tannery industry. Conventional treatment and disposal of tannery sludge are based mainly on incineration and land filling. The aim of this study was to evaluate the effects of a pre-treatment process composed of aerobic stabilisation, compaction and drying for a sustainable land filling of tannery sludge. The process produced a reduction of volume mass and biodegradability of treated sludge. Results also demonstrated a reduced leachability of organic and inorganic compounds from treated sludge. The pre-treatment process could allow extending land fill life time due to lower amounts of tannery sludge to be disposed off, minimise long terms land fill emissions and obtain a state of carbon sink for tannery sludge land filling.

#### 1.3.4 Advanced (tertiary) treatment

In certain cases, despite extensive physical-chemical and biological treatment in a well designed ETP, the quality of the final effluent does not meet the promulgated discharge limits. The usual culprit is the recalcitrant COD, i.e., compounds that the micro-organisms present in the floc are unable to decompose.

In such cases, it is necessary to resort to additional, usually more sophisticated and rather expensive treatments such as mineralization of organic compounds by oxidation with  $H_2O_2$  in the presence of ferrous sulphate (Fenton process and its derivatives). Ozonation is sometimes included not so much to kill potentially harmful micro-organisms but to destroy part of the residual COD.

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##### 1.3.4.1 REVERSE OSMOSIS

Like demineralization plant there is another stage of water treatment which is known as reverse osmosis plant. RO plant uses the process known as reverse osmosis

to produce salt-free water. Osmosis is a process in which only the solvent molecules pass through a semi-permeable membrane from higher solvent density to lower solvent density (i.e. from solution of lower density to the solution of higher density).

Osmotic pressure :- It is the minimum pressure that should be applied on the higher density solution so that no osmosis takes place through the semi-permeable membrane is called the osmotic pressure ( $\pi$ ).

$$\pi = iCRT$$

Where,

C is concentration of solution,

R is universal gas constant,

T is temperature in Kelvin scale,

i is van't Hoff's factor, different for different solutions.  $i = 1$  for infinitely dilute solution.

Hence osmotic Pressure is a function of temperature.

Steam air pre-heater require some steam which will reduce the efficiency of the power plant. The procedure is described below:

(1) Sodium hypochlorite ( $NaOCl$ ) is injected to raw water to kill the algae or bacteria present in the raw water. Otherwise they may cause harm to the multi grade-filter (MGF).

(2) The multi-grade filter is the primitive type of filter where sand, stone-chips, stones are used in stacks to remove the large size suspended particles from the raw water.

(3) The net filter again removes medium-size suspended particles, where the raw water passes through the net minute vents.

(4) Then by ultra-filtration very small suspended particles are removed. After long usage of ultra-filtration unit, it requires back-wash, and then it is back-washed with water & three chemicals, viz. HCL, NaOH & NaOCl (Sodium Hypochlorite). HCl Removes iron by dissolving it. It also removes the basic salts those are rejected on UFU. NaOH ← It helps to remove acidic salt. NaOCl ← To kill algae and bacteria inside the UFU.

(5) After ultra-filtration the water is stored into RO feed tank & then pumped with RO feed pump of Reverse Osmosis Plant. In the channel the water is mixed with HCL (for pH controlling, as the water coming from RO plant or RO permeate water should have pH around 6.0) and SMBS (sodium meta bi-sulphate) [ $Na_2S_2O_5$ ]. Due to the presence of sodium hypochlorite the water is chlorinated. To remove excess chlorine SMBS is used. If excess chlorine is not removed then the semi-permeable membrane may get

damaged. It is also mixed with anti-scaling reagent (AS), which reacts with those chemicals which form scale inside the channel.

(6) Then the water is passed through micro-cartridge filter (MCF) which removes the other suspended particles & the precipitate formed by the reaction of anti-scaling reagent with the scaling chemicals.

(7) In the this stage of boiler feed water treatment the water is fed to RO unit by H/P pump, where after successive filtration by 1<sup>st</sup> & 2<sup>nd</sup> stage RO it is fed to degasser unit.

(8) After degasification the water is passed through D/M plant MB (mixed bed) resin & stored into D/M water storage tank.

## CONCLUSION

This paper discusses about some of the effluent characteristics of tannery wastewater and the biological and advanced treatment process available for the treatment and disposal of tannery wastewater. Normally the floating materials can be removed by coarse screen. With less detention time, some of the particles can be removed in grit chamber. Then the sedimentation process as primary treatment removes the particles which are in suspension from the influent. Biological treatment method appears to be a better choice for the removal of colour and organic content. In this process, if biological method like aerated lagoon is used to treat the bio degradable organic matter, then 90% of BOD is removed from the wastewater. Generally, the tannery wastewater has some dissolved content; using reverse osmosis the dissolved content is removed. Further the treated water can be recycled to the same tannery industry for the use of tanning process in which the TDS content is low. By this process, the treatment can achieve zero effluent discharge standards. Thus the application of combined process of aerated lagoon with reverse osmosis process to treat tannery wastewater would give satisfactory results compared to individual treatment process.

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