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Environmental Effects ofthe Main Constituents of Tannery Effluents (A Review)

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ABSTRACT:*Tannery effluent is among one of the hazardous pollutants from industry.* *The major public concern over tanneries has traditionallybeen about odours and water pollution from untreateddischarges. However, with industrialization major pollutants associated with the tanningindustry include chlorides, tannins, chromium, sulphate andsulphides in addition to trace organic chemicals andincreasing use of synthetic chemicals such as pesticides, dyesand finishing agents, as well as from the use of newerprocessing chemical solvents. Thesesubstances are frequently toxic and persistent, and affect bothman and the environment. This study reviews major constituent of tannery waste and their effect on environment*.

KEY WORDS :*Tannery effluents; Toxic effects; environment*.

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I. INTRODUCTION

Tanning is one of the oldest industries in the world. During ancient times, tanning activities were organized to meet the local demands of leather footwear, drums and musical instruments. With the growth of population, the increasing requirement of leather and its products led to the establishment of large commercial tanneries. Two methods areadopted for tanning of raw hide andskin viz., vegetable tanning and chrome tanning.There is the widespread misperception that vegetable tanning is environmentally harmless (inreality its effluents have very high, difficult to treat COD); this publication focuses on combined chrometanning, which is by far the most prevailing leather tanning method (UNIDO,2011).

The production processes in a tannery can be split into four main categories:

(1) Hide and skin storage and beam house operations, (2) tanyard operations, (3) post-tanning operations and (4) finishing operations. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product. As shown in table 1, tanningindustry has one of the highest toxic intensity per unit of output (Khan et al., 1999). During tanning process at least about 300 kg chemicals are added per ton of hides 0 (Rajasimman,*et el*.,2007)Tannery effluent is among one of the hazardous pollutants from industry**.** The major public concern over tanneries has traditionallybeen about odours and water pollution from untreateddischarges. Important pollutants associated with the tanningindustry include chlorides, tannins, chromium, sulphate andsulphides as addition to trace organic chemicals andincreasing use of synthetic chemicals such as pesticides, dyesand finishing agents, as well as from the use of newerprocessing chemical solvents, (Sekaran,*et.el.*,1998).These substances are frequently toxic and persistent, and affect bothhuman health and the environment (Rajamani,*et. el.*,1998)

II. AVERAGE MAJOR POLLUTION LOAD OF TANNERY EFFLUENT

Parameter	Unit	Average total pollution load	Typical limits, surface waters
BOD_5	mg O_2/l	2,000	30-40
COD	mg O_2/l	4,000	125-250
Suspended solids (SS)	mg/l	2,000	35-100
Cr^{3+}	mg Cr/l	150	1.5-2.0
S^{2-}	mg S/l	160	1.0-2.0
Total nitrogen (TKN)	mg N/l	160	100
Cl^-	mg Cl/l	5,000	Locally specific
SO_4^{2-}	mg SO_4/l	1,400	Locally specific
Oil and grease	mg/l	130	Locally specific
TDS*	mg/l	10,000	Locally specific
pH		6-9	5.5-9.5

Table1: Concentration in combined raw effluent(UNIDO,2011)*The main constituent of total dissolved solid are Cl^- and sulphate(SO_4^{2-})

Solids

1. Suspended solids

Suspended solids present in effluents are the quantity of insoluble matter contained in thewastewater. These insoluble materials cause a variety of problems when discharged; essentially, there aretwo types of solids distinguished by significantly different characteristics.

a. Solids with a rapid settling rate (settleable solids)

If wastewaters are to be treated in sewage works or to undergo traditional effluent treatment, the mainproblems that arise are due to the large volume of sludge that forms as the solids settle. Sludge oftencontains up to 97% water, giving rise to huge quantities of "light" sludge. Even viscous sludge has awater content of about 93% and can easily block sumps, sludge pumps and pipes.Sludge haveto be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources.Even a thin layer of settled sludge can become a blanket that deprives sections of the river or lake bed ofoxygen. As a result, aquatic life dies and decomposition sets inBuljan, (2005)**.**

b. Semi-colloidal solids

Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out even if theeffluent is left to stand for a considerable period of time. Semi-colloidal solids will not directly cause asludge problem. They can be broken down over an extended period by bacterial digestion and producesolids, which will eventually settle (Rajasimman,*et el*.,2007).

2. Gross solids

Gross solids are larger than those a sampling machine can handle; hence they are not measured. Their. presence, however, is clear to see and the dangers they pose are fully recognized. The waste componentsthat give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarsebar screens set in the wastewater flow. However, if they emerge from the factory, they settle out very rapidly. Major problems can develop if these materials settle in the pipes since they lead to blockages. Theproblems can be very serious when blockages occur in inaccessible piping. The cost of replacing burned-outmotors or broken rotors is high. If discharged into gullies, ditches or water courses, the debris rapidlyaccumulates causing blockages and leading to stagnation(**UNEP-UNIDO, 1991).**

Nitrogen

Nitrogen is contained in several tannery effluent components. Sometimes, these sources have to be differentiated.

Total Kjeldahl nitrogen (TKN)

Several tannery effluent components contain nitrogen as part of their chemical structure. The most commonchemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials(from liming/unhairing operations).These sources of nitrogen pose two direct problems to environment:

a. Plants require nitrogen in order to grow, but the high levels released by substances containing nitrogenover-stimulate growth. Water-based plants and algae grow too rapidly, whereupon waterways becomeclogged and their flow is impaired. As the plants die, a disproportionately high amount of organic matter hasto be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobicbacteria die and ultimately anaerobic conditions develop(Chung, et el.,2004).

b. The nitrogen released through protein breakdown and the deliming process is in the form of ammonia.Bacteria can convert the latter over several stages into water and nitrogen gas, which is ultimately releasedinto the atmosphere.These breakdown products are non-toxic, yet large amounts of oxygen areneeded in the process. If oxygen demand is greater than the level supplied naturally by the body of water,toxic anaerobic conditions can rapidly develop. Combining intensive aerobic and anaerobic biological treatment can break down the nitrogenous compounds. The oxygen demand is very high, thus leading to correspondingly high operational and energycosts. Calculations show that, with typical tannery effluent, some 40% of oxygen requirements are spenton removing the nitrogen component(UNIDO,2011; Chung,*et el.*,2004).).

Sulphides (S_2^-)

The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphideand the breakdown of hair in the unhairing process. Under alkalineconditions, sulphides remain largely in solution. (Sekaran,*et.el.*,1998). When the pH of the effluent drops below 9.5, hydrogensulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterizedby a smell of rotten eggs, a severe odour problem occurs.In its toxicity, hydrogen sulphide is comparable to hydrogen cyanide; even a low level of exposure to thegas induces headaches and nausea, as well as possible eye damage. As shown, in table 2, at higher levels, death can rapidly setin, and countless deaths attributable to the build-up of sulphide in sewage systems have been reported.Hydrogen sulphide gas is also soluble.(Sekaran,*et.el.*,1998). When absorbed, weak acids can form and cause corrosion. Thisweakens metal roofing, girders and building supports. In sewers, major problems can arise as metal fittings, structural reinforcements and piping corrode.If discharged into surface water, even low concentrations pose toxic hazards. Sulphides can be oxidizedinto non-toxic compounds by certain bacteria in rivers; however, thiscreates oxygen demand that, ifexcessive, can harm aquatic.

Exposure ppm	Time	Impact on unprotected person
0.03	No time limit	No effect
0.08-2.0	No time limit	(Mal)odour threshold
10	Up to 8 hours	No effect
15	Up to 15 minutes	Threshold limit value
15-200	Up to 15 minutes	Headache, nausea, general weakness, pain in legs
200-500	One minute	Irritation of nose and throat, vertigo, blurring of vision, loss of consciousness lasting a few minutes
500-900	One minute	Profound coma, convulsions, disorientation after recovery
> 900	One minute	Instant coma and death

Table 3 poisoning effect o hydrogen sulphide(UNIDO,2011). ppm = part per million

Neutral salts

Two common types of salts are to be found in tannery effluent:

1. Sulphates $(SO_4)^{2-}$

Sulphates are a component of tannery effluent which emanates from the use of sulphuric acid or productswith a high (sodium) sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-productof their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate, as domany synthetic re-tanning agents (Sekaran,*et.el.*,1998).Removing the sulphide component from effluent by aeration creates an additional source, since theoxidation process produces a whole range of substances, including sodium sulphate. Sulphates can beprecipitated by calcium-containing compounds to form calcium sulphate that has a low level of solubility. However,problems arise with soluble sulphates, for two main reasons:

a. Sulphates cannot be removed completely from a solution by chemical means, but under certain biologicalconditions, it is possible to remove sulphate from a solution and bind the sulphur into micro-organisms.Generally, however, the sulphate either remains as sulphate or is broken down by anaerobic bacteria toproduce malodorous hydrogen sulphide. This process occurs very rapidly in effluent treatment plants,sewage systems and water courses, if effluents remain static. This bacterial conversion to hydrogen sulphidein sewage systems results in the corrosion of metal parts, and unless it is sulphate-resistant, concrete willgradually erode.

b. If no breakdown occurs, there is the risk of increasing the total concentration of salts in surface watersand groundwater(Chung,*et el.*,2004).

2. Chlorides (Cl^-)

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantitiesof common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, itis not affected by effluent treatment and nature, thus remaining as a burden on the environment.(Koteswari,2003).Considerable quantities of salt are produced by industry and levels can rapidly rise to the maximum levelacceptable for drinking water. Increased salt content in groundwater, especially in areas of high industrialdensity, is now becoming a serious environmental hazard.Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases throughevaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system andmay ultimately end up in the groundwater(Rajamani,et el., 1998 ; Srivastava,*et. el.*,2008).

Oils and grease

In leather manufacture, natural oils and grease are released from within the skin structure. If fat liquorexhaustion is poor, some fatty substances may be produced through inter-reaction when wastewaters mingle.Floating grease and fatty particles agglomerate to form "mats," which then bind other materials, thuscausing a potential blockage problem especially in effluent treatment systems Rajamani,(1997). If the surface waters arecontaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If thesefatty substances accumulate, they create a very high oxygen demand on account of their bio-degradability (Koteswari,2003).

pH value

Acceptable limits for the discharge of wastewaters into both surface waters and sewers vary, ranging frompH 5.5 to pH 10.0 (Rajasimman,*et el.*,2007) Although stricter limits are often set, greater tolerance is shown towards higher pH values since carbon dioxide from the atmosphere or from biological processes in healthy surface watersystems tends to lower pH levels very effectively to neutral conditions. If the surface water pH shifts toofar either way from the pH range of 6.5-7.5, sensitive fish and plant life may be lost Srivastava,*et. el.,(*2008)Municipal and common treatment plants prefer discharges to be more alkaline to reduce the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulphide evolution isminimized. When biological processes are included inthe treatment, the pH is lowered to more neutralconditions by carbon dioxide (Srivastava,*et. el.*,2007).

Chromium compounds

Metal compounds are not biodegradable. They can thus be regarded as long-term environmental features.Since they can also have accumulative properties, they are the subject of close attention. Two forms ofchrome are associated with the tanning industry, and their properties are often confuse.

1. Chrome 3^{3+} (trivalent chrome, chrome III)

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the re-tanningsystem and is displaced from leathers during re-tanning and dyeing processes. This chrome is dischargedin soluble form; however, when mixed with tannery wastewaters from other processes (especially ifproteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, whichadd to sludge generation.(Ates,*et. el.*, 1997).
Very fine colloids are also formed which are then stabilized by the chrome – in effect, the protein has beenpartially tanned. The components are thus highly resistant to biological breakdown, and the biologicalprocess in both surface waters and treatment plants is inhibited.Once successfully broken down, chromium hydroxide precipitates and persists in the ecosystem for anextended period of time. If chrome discharges are excessive,**it** might remain in the solution.Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish lifeand possibly inhibiting photosynthesis(Onyancha, *et. el.*, 2008).

2. Chrome 6+ (hexavalent chrome, chrome VI)

Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. However, tannery effluents are unlikely to contain chromium in this form(Onyancha, *et. el.*, 2008).

III. CONCLUSION

Tannery effluent chemical are obviously toxic to environment. However, It is possible to decrease significantly the pollution load, namely:COD and BOD5 by more than 30%, sulphides by 80-90%, ammonia nitrogen by 80%, total (Kjeldahl) nitrogen by50%, chlorides by 70%, sulphates by 65%, and chromium by up to 90% , by applying industrially proven low-waste advanced methods such as the use of salt-free preserved rawhides and skins, hair-save liming, low-ammonia or ammonia-free deliming and bating, advanced chromemanagement systems, etc.,Yet, despite all preventive measures, there is still a considerable amount of pollution load to be dealt withby end-of-pipe methods.

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